

COMPLEX INTERACTIONS OF LONG-TERM PATTERNS IN DISSOLVED ORGANIC
CARBON WITH REGIONAL AND GLOBAL VARIABLES IN EASTERN CANADIAN
LAKES

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By

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Abstract

Dissolved organic carbon (DOC) is an important water quality parameter that can affect many physical, chemical and biological processes in aquatic ecosystems. The long-term patterns in ice-free DOC in 49 eastern Canadian lakes from four sites were re-examined with a ~35-year dataset. Long-term patterns in DOC were synchronous in lakes within a site (Brien's test, $p > 0.05$), but not across sites ($p \leq 0.04$), except between Kejimikujik and Yarmouth. Hence, these two sites were pooled into a single Nova Scotia site (NS). Increases in DOC concentration in Dorset lakes were evident between 1997 and 2015 (increase of $0.12 \text{ mg L}^{-1} \text{ year}^{-1}$, $r^2 = 0.68$, $p < 0.001$). Similar increases were also apparent in NS between 2000 and 2015 (increase of $0.11 \text{ mg L}^{-1} \text{ year}^{-1}$, $r^2 = 0.34$, $p = 0.02$). Although the long-term DOC concentrations at the ELA lakes showed an increasing trend between 1983 and 2000 (increase of $0.10 \text{ mg L}^{-1} \text{ year}^{-1}$, $r^2 = 0.39$, $p = 0.005$), no evidence of an increase or a decrease was detected between 2001 and 2015 ($r^2 = 0.02$, $p = 0.59$). The long-term relationships in ice-free DOC concentration and four regional and three global variables were examined. Declining SO_4 deposition was the most important factor that explained the DOC increases in the last two decades in Dorset and NS. Summer precipitation also explained a significant amount of variation in DOC at these two sites. Interestingly, some global variables (i.e., North Atlantic Oscillation and Pacific Decadal Oscillation) emerged as important explanatory variables for the first time in Dorset and NS. The negative association between DOC and NAO was explained indirectly by the significant correlations between North Atlantic Oscillation and temperature. However, such correlations were not found between Pacific Decadal Oscillation and regional climate variables. Declining SO_4 deposition was also found to be the most important explanatory variable at the ELA. However, despite a declining SO_4 deposition pattern throughout the study period, a rise in DOC concentration was not evident between 2001 and 2015 at the ELA. Long-term DOC patterns in the ELA lakes may have reached an equilibrium in 2000, when declining SO_4 deposition could not cause any further increase in DOC. Absence of an increase or decrease in DOC concentration after 2000 may be attributed to additional acidity from an increase in nitrogen (N) or ammonium (NH_4^+) deposition at the ELA.

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List of Abbreviations

AIC - Akaike's information criterion
Al - Aluminum
AWMN - Acid Waters Monitoring Network
C - Carbon
Ca - Calcium
Cd - Cadmium
C-DOC - Chromophoric dissolved organic carbon
Cl - Chlorine
CO - Carbon monoxide
CO₂ - Carbon dioxide
Cu - Copper
DESC - Dorset Environmental Science Center
DIC- Dissolved inorganic carbon
DIN – Dissolved inorganic nitrogen
DOC - Dissolved organic carbon
DOM - Dissolved organic matter
ELA - Experimental Lakes Area
ER - Evidence ratio
Fe - Iron
H₂CO₃ - Carbonic acid
Hg - Mercury
HS - Humic substances
K- Potassium
KNP - Kejimikujik National Park
MeHg - Methylmercury
Mg - Magnesium
MLR - Multiple linear regression
N - Nitrogen
NAO - North Atlantic Oscillation

NH₄ - Ammonium
NREL - National Renewable Energy Laboratory
NS - Nova Scotia
PAR - Photosynthetically active radiation
Pb - Lead
PDO - Pacific Decadal Oscillation
POC - Particulate organic carbon
PPTN - Precipitation
ROS - Reactive oxygen species
SD - Sulfate deposition
SO₄ - Sulfate
SOI- Southern Oscillation Index
SO_x - Sulfur oxides
T - Temperature
TN – Total nitrogen
TP - Total phosphorus
TSR - Total solar radiation
U - Uranium
U.K. - United Kingdom
U.S. - United States
UVR - Ultraviolet radiation
 w_i - Akaike's weight
Zn - Zinc

CHAPTER 1. INTRODUCTION

1.1 Dissolved organic carbon (DOC)

Carbon (C) is categorized into two types, inorganic carbon (e.g., CO_2 and H_2CO_3) and organic carbon. These two types of carbon can be converted from one to the other through different processes. Carbon mineralization is a complex process in which organic substances are converted into inorganic forms by bio-mineralization or photo-mineralization or both (Tranvik et al. 2009; Butman et al. 2015). Different stages in the degradation processes include chemical changes, physical fragmentation and finally release of inorganic nutrients. On the other hand, the process in which inorganic carbon is converted into organic carbon by living organisms is called carbon fixation or carbon assimilation. Photosynthesis is an example of a carbon fixation process where inorganic carbon is reduced and converted into organic form using the energy from sunlight. Organic carbon can include both living and non-living materials. Aquatic organic carbon can be further classified into particulate organic carbon (POC) and dissolved organic carbon (DOC). The portion of organic carbon that can pass through a filter of 0.45 or 0.2 micrometers pore size is termed DOC (Thurman 1985; Zsolnay 2003; Xu and Guo 2017). Although DOC and DOM (dissolved organic matter) are often used interchangeably, in actuality about 67% of DOM is DOC (Bolan et al. 2011). The major portion of DOC (60-90%) is composed of humic substances (HS; Sachse et al. 2005) that are relatively complex molecules compared to non-humic substances (e.g., carbohydrates, lipids and amino acids). Humic substances (HS) have high molecular weight and their chromophoric properties often cause brownification in waterbodies (Findlay and Sinsabaugh 2003; Roulet and Moore 2006). DOC also contains fulvic acids which are water soluble and have low molecular weight. DOC

represents the greatest organic carbon pool in lakes compared to other pools like heterotrophic bacteria, phytoplankton, zooplankton and fish (Prairie 2008).

1.1.1 Types of DOC

Generally, the two main sources of DOC to lakes are from terrestrial sources (Aitkenhead-Peterson et al. 2003) and within-lake sources like phytoplankton, benthic algae, and aquatic macrophytes (Bertilsson and Jones 2003; Lennon 2004). DOC that is derived from in-lake processes is called autochthonous DOC (Findlay and Sinsabaugh 2003). DOC that comes from sources outside of the lake (e.g., upstream or terrestrial sources) is called allochthonous DOC (Wetzel 2001; Reche and Pace 2002; Steinberg et al. 2006).

Autochthonous DOC is usually produced from autotrophic and heterotrophic in-situ activities (Kritzberg et al. 2004; Guilemette and del Giorgio 2012). Unlike terrestrial DOC, autochthonous carbon compounds typically lack chromophoric structures and may not impart color to the water. Autochthonous DOC usually consists of lower molecular weight compounds like amino acids, lipids, proteins and polysaccharides, and is considered more bioavailable for microbial use (McDonald et al. 2004; Farjalla et al. 2009; Fonte et al. 2013). As a result, autochthonous DOC is preferentially utilized by bacteria compared to allochthonous DOC (Bertilsson and Jones 2003; Kritzberg et al. 2006), and supports a greater bacterial biomass and rates of productivity (Karlsson et al. 2015). Autochthonous DOC may consist of 5-20% of total DOC in streams but this can increase to almost 90% in certain situations (Bertilsson and Jones 2003; Kritzberg et al. 2004). In general, allochthonous DOC inputs are considered the main sources of DOC in aquatic systems. However, lakes with abundant submerged macrophytes can have significant autochthonous DOC (DeMarty and Prairie 2009; Obrador and Pretus 2012).

Allochthonous DOC is typically the outcome of throughfall, root exudate, leaf and root litter, primary and secondary metabolites of microorganisms and dissolved atmospheric dust and gases (Aitkenhead-Peterson et al. 2003). Allochthonous DOC is usually exported to aquatic systems by groundwater and surface water (Solomon et al. 2015). Export of allochthonous DOC from terrestrial systems to inland waters has been estimated at $3 \text{ Pg C m}^{-2} \text{ year}^{-1}$ (Tranvik et al. 2009). DOC export can be influenced by many factors including climate, hydrology and land use (Mattsson et al. 2009; Wu et al. 2011; Stanley et al. 2012; Kellerman et al. 2014; Laine et al. 2014; Aitkenhead-Peterson and Steele 2016). Before entering lakes, the majority of allochthonous DOC is processed as it passes through soils (Wetzel 2001). This produces HS and colored polymers of large molecular weight. Therefore, allochthonous DOC is often termed colored DOC or chromophoric DOC (C-DOC) which imparts a yellow to brown color to the water (Osburn and Morris 2003; Roulet and Moore 2006). Humic substances (HS) are complex and do not have a standard chemical formula compared to non-humic substances (Reitsema et al. 2018). HS consist of aromatic and aliphatic components that include ketone, carboxyl, amide and other functional groups (Leenheer and Croue 2003). Moreover, a sub-division of HS based on the water solubility at different levels of acidity includes humic acids, fulvic acids and humin (Pettit 2004, McDonald et al. 2004). Humic acids have the highest molecular weight of 1500-5000 Da in natural waters and are usually soluble at a pH below 2 (Malcolm 1990; Reitsema et al. 2018). Fulvic acids, on the other hand, are soluble at any pH in natural waters and have molecular weights ranging from 600 to 1000 Da (Malcolm 1990; Reitsema et al. 2018). The humin portion of HS is not soluble in water at any pH (McDonald et al. 2004). Fulvic acids contain more carboxyl groups and oxygen atoms compared to humic acids that contain more phenolic and aromatic groups with longer aliphatic chains (Reitsema et al. 2018). As a result,

humic acids are less polar than fulvic acids and less soluble in water. Allochthonous DOC was thought to be less susceptible to biological mineralization compared to non-humic substances (Wetzel 2001; Kritzber et al. 2004; Mitrovic and Baldwin 2016) because of its complex structure and larger molecular weight (Appiani et al. 2014). However, subsequent studies have found that allochthonous DOC is less recalcitrant than previously assumed (Tank et al. 2010; Tanentzap et al. 2014). Through photodecomposition, ultraviolet radiation (UVR) can transform large molecular weight compounds to simpler organic compounds (e.g., small fatty acids such as acetic, formic and citric acid) that are readily metabolized by microorganisms (Tranvik and Bertilsson 2001; Belanger et al. 2006; Laurion and Mladenov 2013).

1.2 Important roles of DOC

1.2.1 Source of energy

DOC is an important component of the energy budget of lake food webs (Mattsson et al. 2005; Karlsson et al. 2012; Robbins et al. 2017). In general, autochthonous DOC is more labile and therefore, it can increase bacterial biomass (Wilcox et al. 2005) and ecosystem respiration (Johnson et al. 2012; Oviedo-Vargas et al. 2013; Robbins et al. 2017). Autochthonous DOC contribution is generally greater in nutrient-rich lakes (Perga et al. 2006). On the other hand, allochthonous DOC usually contributes most in low-productive humic lakes (Solomon et al. 2011; Karlsson et al. 2003, 2012; Figueroa et al. 2016). Nutrients released from allochthonous DOC through the photodecomposition processes can stimulate primary productivity (Klug 2002; Sereda et al. 2012; Kissman et al. 2013). Moreover, allochthonous DOC can support the consumers in benthic and pelagic habitats by increasing bacterial consumption (Karlsson et al. 2004; Berggren et al. 2010). Karlsson et al. (2012) reported that 85% of community respiration

in a humic lake relied on allochthonous DOC (DOM) which supported approximately half of zooplankton, macrozoobenthos and fish biomass. Wilk-Wozniak et al. (2014) reported that rotifer production in a reservoir was dependent on the microbial food web which was largely supported by allochthonous DOC input.

1.2.2 Attenuation of solar radiation

UVR can cause a variety of ecological impacts in aquatic systems (ACIA 2005; Hader et al. 2015). Chromophoric DOC (C-DOC) can affect optical properties of lake water including underwater UV exposure (Vincent et al. 2007; Forsstrom et al. 2015). Therefore, C-DOC reduces the detrimental effects of UVR through attenuation (Rautio and Korhola 2002; Maloney et al. 2005; Bracchini et al. 2006; Rautio et al. 2009; Karlsson et al. 2009; Nevalainen et al. 2015). Chromophoric DOC (C-DOC) can also attenuate photosynthetically active radiation (PAR; Thrane et al. 2014) and hence, decrease photosynthesis through light limitation (Meyer et al. 2016). As a result, an increase in C-DOC may alter the balance between algal photosynthesis and respiration (von Einem and Graneli 2010; Kritzberg et al. 2014, Kelly et al. 2014) and therefore, may restrict primary production (Karlsson et al. 2009; Jones et al. 2012; Godwin et al. 2014; Thrane et al. 2014; Seekell et al. 2015).

1.2.3 Effects on lake transparency and thermal properties

Through attenuation of solar radiation, C-DOC can greatly affect water column transparency (Gunn et al. 2001; Williamson et al. 2014, 2015; Pilla et al. 2018), lake thermal stratification and mixing depths (Keller et al. 2006; Persson and Jones 2008; Read and Rose 2013; Strock et al. 2017). As a result, DOC can influence water chemistry and the productivity of lake ecosystems (Berger et al. 2007). Strock et al. (2017) attributed the decrease in water

transparency in Maine lakes to an increase in DOC concentration. They also associated a reduction in the thickness of the epilimnion of some lakes with a concomitant increase in DOC. A decrease in water transparency due to an increase in DOC can cause more heat to be absorbed in the epilimnion that may lead to a shallower thermocline (Persson and Jones 2008). In a study of two lakes over a 27-year period, Williamson et al. (2015) reported that an increase in DOC concentration resulted in a decrease in water transparency and an increase in surface water temperature by 2-3°C. Similar consequences of reduced transparency due to an increase in DOC have also been reported elsewhere (Rose et al. 2016; Pilla et al. 2018).

1.2.4 Heavy metal toxicity

DOC can bind with many metal cations and hence, affect the speciation of trace heavy metals and their bioavailability and toxicity. Humic substances (HS) in DOC have a complex combination of carboxylated and fused alicyclic structures that can be strong metal binding ligands (Hetkorn et al. 2006; Yang et al. 2009). Most metal binding occurs at carboxylic and phenolic sites. Usually carboxylic groups are associated with low metal affinity sites, and phenolic groups are associated with high affinity sites (Baken et al. 2011). Some DOC may also form metal binding ligands like aminopolycarboxylates and sulfides (Knepper 2003; Sarathy and Allen 2005). Because of this large site diversity, both quantity and quality of DOC can affect metal binding characteristics. The association between DOC (DOM) and the solubility and toxicity of various metals are well documented (Yan et al. 2013; Chakraborty et al. 2014; Gao et al. 2015; Yan et al. 2016; Hu et al. 2017; Santore et al. 2018). For example, methyl-mercury (MeHg) is potentially harmful to its consumers (Scheulhammer et al. 2007; Driscoll et al. 2013). DOC can affect the mercury (Hg) cycle and photochemical degradation of MeHg through complexation (Ravichandran 2004; Lehnher and Louis 2009; Klapstein et al. 2018). Several

studies have reported a positive relationship between DOC concentration and Hg (Driscoll et al. 1995; Chasar et al. 2009; Braaten et al. 2014). However, more recent studies have found that Hg availability for biological uptake can be reduced at greater DOC concentrations (Tsui and Finlay 2011; French et al. 2014; Jeremiason et al. 2016; Braaten et al. 2018). French et al. (2014) reported an increased accumulation of both total Hg and MeHg in aquatic invertebrates at DOC concentration below 8.6 mg L⁻¹ in tundra lakes, when Hg was associated with low molecular weight fulvic acids. However, Hg bioaccumulation decreased drastically when DOC concentration was greater than 8.5 mg L⁻¹ because in greater DOC concentration, Hg adsorption was mostly associated with binding sites on humic acids that are not readily bioavailable. A similar interpretation was also given by Braaten et al. (2018). They reported that an increase in DOC was associated with an increase in Hg concentrations in boreal lakes. However, bioaccumulation of MeHg in fish was reduced when DOC concentration was greater. DOC may also affect the toxicity of other important metals including copper (Cu; Gillis et al. 2010; Cooper et al. 2014; Taylor et al. 2016), aluminum (Al; Trenfield et al. 2012; Gensemer et al. 2018), cadmium (Cd; Burnison et al. 2006), lead (Pb; Lamelas and Slaveykova 2007; Mager et al. 2011), zinc (Zn; Heijerick et al. 2003; Ouyang et al. 2017) and uranium (U; Trenfield et al. 2011).

1.2.5 The relationship between DOC and watershed characteristics

Allochthonous DOC is primarily derived from the upstream watersheds and therefore, reflects watershed characteristics (Mosher et al. 2010; Yamashita et al. 2011; Cawley et al. 2014; Lu et al. 2013; Lu et al. 2014). For example, the quantity of DOC is proportional to the percentage of wetlands in a watershed (Dillon and Molot 1997; Wetzel 2001; Richardson et al. 2010, Hosen et al. 2018). A greater allochthonous DOC concentration in lakes is usually

associated with larger watersheds (Mulholland 2003; Frost et al. 2006). Moreover, the composition of bioavailable DOC has been reported to reflect unique features in Arctic river watersheds (Kaiser et al. 2017). Furthermore, DOC quantity and quality may also provide information on other watershed properties including land use (Wilson and Xenopoulos 2009; Williams et al. 2010; Saniewska et al. 2018), soil quality (Jones et al. 2014) and wetland types (Hosen et al. 2018).

1.3 Factors affecting the concentration and pattern in DOC

1.3.1 Local variables

Several watershed characteristics can affect the quality and quantity of DOC. For example, DOC concentration in aquatic systems can be affected by soil properties of the surrounding watersheds (Scott and Rothstein 2014; Singh et al. 2018; Li et al. 2018; Wickland et al. 2018; Bertolet et al. 2018). The quantity and composition of DOC in lakes and streams can also be affected by hydrological characteristics that may include magnitude of storm events, transitions in hydrologic cycle, seasonal variation, discharge conditions and flow pathways (Inamdar et al. 2011; von Schiller et al. 2015; Voss et al. 2015; Guarch-Ribot and Butturini 2016; da Costa et al. 2017). Most DOC export from allochthonous sources usually takes place during hydrologic events that are associated with high discharge (e.g., storm and snowmelt). For example, Raymond and Saiers (2010) reported that events with greater discharge ($> 1.38 \text{ cm day}^{-1}$) were responsible for most annual DOC export in 30 small eastern United States (U.S.) forested watersheds. However, antecedent hydrological conditions were also reported to be important in boreal lakes (Agren et al. 2010; Winterdahl et al. 2011). Moreover, as noted earlier, watershed properties like the proportion of wetlands in a watershed can affect DOC concentration and

quality. Dynamics of DOC can also be affected by the characteristics of forests in the watershed (Yan et al. 2015; Xiao et al. 2016; Camino-Serrano et al. 2016; Lee et al. 2018; Kooch and Haghverdi 2018). For example, DOC concentration in coniferous forests can be greater than that of broadleaved forests (Froberg et al. 2011; Camino-Serrano et al. 2014). This is because of the slower decomposition rate of coniferous litter, which in turn, results in a thicker litter layer in coniferous forests (Froberg et al. 2011; Hansson et al. 2011). The thicker the litter layer, the more infiltrating water is likely to be in contact with organic matters (Borken et al. 2011). This will increase the dissolvability of organic molecules into DOC. In addition, the type of land use in watersheds is another important local factor that may influence allochthonous DOC in lakes (Graeber et al. 2012; Manninen et al. 2018; Nobrega et al. 2018; Saniewska et al. 2018). For example, studies have reported an increase in DOC concentration in waterbodies that have a large proportion of agricultural land in their catchments (Mattsson et al. 2005). Greater organic matter solubility in agricultural lands has been attributed to the application of organic fertilizers (Zsolnay and Gorlitz 1994). An increase in fertilizer application can cause an increase in organic dry matter production and in turn, greater organic matter losses (McTiernan et al. 2001). Different crop production practices in agricultural lands may also affect soil organic carbon concentrations (Angers and Eriksen-Hamel 2008; Van Eerd et al. 2014), and subsequently, affect DOC concentrations in lakes and streams. Furthermore, rivers with greater forest cover, meadows and pastures in the catchment may have greater DOC than catchments having just arable lands (Saniewska et al. 2018). Local variables may also include lake characteristics like pH and iron (Fe) concentration, which can strongly influence the biodegradation and mineralization of DOC (Molot et al. 2005; Pace et al. 2012; Timko et al. 2015; Ren et al. 2016; Gu et al. 2017). For example, Fe increases the light absorption by C-DOC and hence, contributes

to dissolved inorganic carbon (DIC) production through changes in the optical properties of C-DOC (Gu et al. 2017). Low pH has been reported to increase this Fe accelerated DIC photoproduction (Gao and Zepp 1998; Wu et al. 2005; Helms et al. 2013). Other important local factors that can affect the production, composition and fate of DOC may include primary production (Miller et al. 2009; Peng et al. 2017; Creed et al. 2018) and wildfires (Revchuk and Suffet 2014; Zhang et al. 2016; Jensen et al. 2017; Evans et al. 2017).

1.3.2 Regional variables

An increase in DOC concentration has been observed in freshwater ecosystems during the last two decades in Europe (Monteith et al. 2007; Erlandsson et al. 2011; Kopacek et al. 2015; Oulehle et al. 2017; Sawicka et al. 2017) and in North America (Monteith et al. 2007; Couture et al. 2012; Williamson et al. 2015; Singh et al. 2016; Strock et al. 2017; Brown et al. 2017). The decline in SO₄ deposition has been identified as the most important factor to explain this increasing pattern (De Wit et al. 2007; Monteith et al. 2007; Erlandsson et al. 2008; Dawson et al. 2009; Haaland et al. 2010; SanClements et al. 2012).

Sulfur oxide (SO_x) emission control programs were initiated in the 1980s as a result of the international concern over the acidification of natural waters and landscapes (Vestreng et al. 2007). Since the implementation of the American and Canadian clean air legislation, SO₄ deposition has declined significantly (Vet et al. 2005; Smith et al. 2011; Vet et al. 2014). This decline in SO₄ deposition has resulted in a decrease in acidity in soil and water, and in turn, an increase in DOC solubility (Krug and Frink 1983; Monteith et al. 2007; Clark et al. 2010; Clark et al. 2011). Declining acidity may increase DOC concentration in lakes primarily by increasing soil pH, and secondarily by decreasing the mobilization of aluminum (Al) that may bind with DOC. In low pH condition, an increase in Al mobility typically increases its binding to organic

ligands, and neutralize negatively charged binding sites. As a result, low pH soil may facilitate an increase in the coagulation of DOC (Tipping and Woof 1991). Conversely, in high pH soils, Al mobilization is reduced, which may result in an increase in DOC solubility in soil (Monteith et al. 2007). Moreover, in less acidic soils, the base cation leakage through cation exchange can be reduced by a lower concentration of hydrogen ions (H^+). Decreased H^+ may also increase the net charge of DOC by decreasing protonation of functional groups (e.g., carboxylic groups). These processes can result in an increase in DOC solubility (Tipping and Hurley 1988; Tipping and Woof 1991; Kalbitz et al. 2000; Ekstrom et al. 2011). In addition, a reduction in acid deposition may result in a reduction in the concentration of multivalent ions (e.g., SO_4^{2-} , Ca^{2+} , Mg^{2+}) which can reduce the ionic strength of the soils (De Wit et al. 2007; Monteith et al. 2007; Hruska et al. 2009). This reduction in ionic strength increases the surface charge and electrostatic repulsion of C-DOC and hence, reduces flocculation, coagulation and precipitation of DOC (Tipping and Hurley 1988; Haaland et al. 2010). Therefore, a decline in ionic strength should increase the export of allochthonous DOC (Evans et al. 1988). Furthermore, a decline in SO_4 deposition should lead to an increase in lake pH, and in turn, a reduction in the acid-enhanced photodecomposition in lakes (Gennings et al. 2001; Kohler et al. 2002; Molot et al. 2005).

Monteith et al. (2007) found that the DOC concentration in 363 lakes and streams in the Northern Hemisphere increased at the same rate at which sulphate (SO_4^{2-}) and sea salt (Cl^-) deposition decreased. Oulehle and Hruska (2009) reported that a long-term increase in DOM between 1969 and 2006 in the Czech Republic was associated with a decline in acidic deposition, particularly SO_4 deposition. Garmo et al. (2014) found that SO_4 deposition declined at their study sites between 1990 and 2008, and this decline was associated with an increase in DOC

concentrations. Similar interpretations were also given by Anderson et al. (2017) in two lakes located in Halifax, Nova Scotia.

Other studies have argued that the long-term increase in DOC was related to climate variables such as temperature, solar radiation and precipitation. Many studies have reported a strong long-term positive relationship between DOC and temperature (Freeman et al. 2001; Worrall and Burt 2007; Couture et al. 2012; Tian et al. 2013; Williams et al. 2016; Chow et al. 2017). Freeman et al. (2001) found that a 65% increase in DOC concentration in freshwaters in United Kingdom (U.K.) over a 12-year period was related to a rise in temperature. Worrall and Burt (2007) reported increases in DOC concentration with an increase in air temperature at 216 sites in Great Britain. Keller et al. (2008) found temperature to be the most important factor that was associated with the patterns in DOC in boreal shield lakes between 1978 and 2003. Tian et al. (2013) also found temperature to be the best explanatory variable in seven major riverine systems in the U.S., where a one-degree Celsius increase in temperature resulted in a 0.48 mg L^{-1} increase in DOC. Similarly, Chow et al. (2017) suggested that DOC concentration in the surface water at Fei-Tsui reservoir in Northern Taiwan was predominantly associated with temperature.

An increase in temperature may increase the DOC concentration by several mechanisms. For example, a rise in temperature can increase DOC concentration in peat soils by increasing decomposition rates via microbial processes (Freeman et al. 2001). This increase in soil DOC can subsequently increase DOC concentration in water.

However, an increase in temperature did not always result in an increase in DOC concentration. A few studies have reported a negative relationship between temperature and DOC. For example, declining flow and increased evaporation from lakes due to higher temperatures will increase water retention times. This, in turn, will increase DOC exposure to

microbial and photochemical removal processes, and consequently, reduce the DOC concentration (Schindler et al. 1996; Schindler 1997). Moreover, Bertolet et al. (2018) reported that a warmer and drier condition can result in a decline in terrestrial DOC inputs to lakes. Furthermore, Shirokova et al. (2013) found that DOC concentration in a humic boreal lake decreased by more than 30% during an unusually hot summer. They suggested that the decrease in DOC was caused by an increase in photodegradation and bacterial mineralization.

Solar radiation has a negative relationship with DOC (Molot and Dillon 1997; Gennings et al. 2001; Molot et al. 2005; Sharpless and Blough 2014; Koehler et al. 2014; Mopper et al. 2015). The negative short and long-term effects of total solar radiation on DOC concentration are well documented (Kopacek et al. 2003; Hudson et al. 2003; Shiller et al. 2006; Zhang et al. 2010; Porcal et al. 2013). Solar radiation can reduce the DOC concentration through photodecomposition. The photodecomposition process is initiated when C-DOC absorbs UVR. Then a series of processes may occur that include photobleaching, photolysis, photodegradation and photo-mineralization. Photobleaching is the loss of chromophoric absorbance and water color (Del Vecchio and Blough 2004; Osburn et al. 2009). Photolysis is the separation of chemical bonds, and photodegradation is the breakdown of DOC into smaller molecules. Finally, photo-mineralization of C-DOC to dissolved inorganic carbon (e.g., CO₂ and CO) occurs when large molecular weight DOC is converted into more labile components (Song et al. 2017) that are subsequently mineralized by microorganisms.

Although short-term studies demonstrated the negative relationship between DOC and solar radiation (e.g., Molot et al. 2005), a strong negative long-term association between DOC concentration and solar radiation was first reported by Hudson et al. (2003) in the Dorset lakes of Ontario. Zhang et al. (2010) found further evidence that total solar radiation was negatively

correlated with the long-term patterns in DOC in a larger dataset of eastern Canadian lakes.

Couture et al. (2012) also reported that solar radiation significantly explained variation in the long-term pattern in DOC in 5 lakes in Quebec between 1989 and 2006.

Precipitation is another important climate variable that strongly influences the long-term patterns in DOC. However, the relationship between DOC and precipitation is often complex. The relationship can be strong or weak and positive or negative, depending on factors like watershed characteristics, the season and sources of DOC. Because there is a very strong relationship between DOC export and runoff (Dillon and Molot 2005), an increase in precipitation can induce a significant loss from the terrestrial organic carbon pool and thus, increase the allochthonous DOC export from terrestrial to aquatic systems (Dillon and Molot 1997; Correll et al. 2001; McClain et al. 2003; Raymond and Saiers 2010; Dyson et al. 2011; Yoon and Raymond 2012; Qiao et al. 2017). Furthermore, DOC concentration in lakes can also increase through the wet deposition of DOC in precipitation (Safieddine and Heald 2017). DOC concentration in precipitation has been reported to range between 0.2 mg L^{-1} and 11.4 mg L^{-1} (Iavorovska et al. 2016).

Hudson et al. (2003) analyzed the long-term patterns in DOC at Dorset as a function of several climate variables and global variables. They found that precipitation was one of the important explanatory variables along with solar radiation. Similar interpretations were also reported by Zhang et al. (2010) in a larger dataset of eastern Canadian lakes. Couture et al. (2012) analyzed the increasing DOC trend in Quebec lakes as a function of a variety of potential explanatory variables. They also found that precipitation was strongly correlated with the long-term DOC pattern. Diodato et al. (2016) reported that DOC concentration was mostly related to precipitation in two pristine boreal lakes in the ELA. Singh et al. (2016) analyzed a 25-year DOC

dataset from a single stream in the U.S. An increase of 165% in DOC from 1997 to 2012 was best explained by an increase in precipitation. Similarly, Pilla et al. (2018) reported that DOC concentration in two temperate lakes increased due to an increase in precipitation.

An increase in precipitation might not necessarily cause an increase in DOC concentration. Heavy precipitation events may dilute lake DOC concentrations. For example, Li et al. (2016) reported a dilution effect of precipitation on DOC in the Tibetan Plateau. This could happen if heavy precipitation events occur in early spring when DOC is still frozen in soils and peats (Schiff et al. 1998; Hudson et al. 2003). This scenario might result in a negative relationship between DOC concentration and winter, or early spring precipitation. Therefore, the relationship between DOC and precipitation may vary in accordance with seasonal variation in precipitation (Qiao et al. 2016; Tiwari et al. 2018).

1.3.3 Global variables

In addition to local and regional variables, some global climate variables have been proposed to influence the long-term patterns in DOC. These variables include the Southern Oscillation Index (SOI), the North Atlantic Oscillation (NAO) and the Pacific Decadal Oscillation (PDO). Global variables do not likely affect lake DOC concentration directly, but they can significantly influence the patterns in regional climate variables like temperature and precipitation (Whitfield et al. 2010; Zhang et al. 2010; Bonsal and Shabbar 2011; Bai et al. 2012; Iles and Hegerl 2017; Fang et al. 2018). This in turn, can affect the long-term patterns in DOC.

SOI is one of the strongest climatic oscillations on Earth. It represents a broad-scale oscillation in the tropical Pacific that can affect the global climate. It is usually measured by the difference in surface pressure anomalies between Tahiti and Darwin (Bonsal and Shabbar 2011). The duration of a SOI cycle is 2 to 7 years (Niedzielski 2014). SOI is commonly associated with

abnormalities in temperature and precipitation, and may cause climate extremes like drought, flooding and tropical cyclones (de Beurs et al. 2018; Fang et al. 2018; de Oliveira et al. 2018; Liu et al. 2018). In Canada, SOI can exert various effects on climate variables. For example, the inter-annual variation in temperature during winter can be affected by SOI (Bonsal and Shabbar 2011). During the negative phase of SOI (El Niño), the frequency and length of winter warm spells have increased, and cold spells have decreased (Shabbar and Bonsal 2004; Bonsal and Shabbar 2011).

NAO is another important climate phenomenon that can influence global climate. It is a major atmospheric oscillation over the North Atlantic that extends from central North America to Europe. NAO is associated with a bipolar seesaw between the Azores High and the Icelandic Low (Xu et al. 2018). Different phases of NAO (i.e., positive and negative) can cause various abnormalities in temperature and precipitation around the globe (Wanner et al. 2001; Sarlak et al. 2009; Pinto and Raible et al. 2012; Ding et al. 2018; Wang et al. 2018; Hao et al. 2018). A negative relationship between NAO and temperature has been reported across eastern Canada (Shabbar et al. 1997; Bonsal et al. 2001; Iles and Hegerl 2017), where NAO explained considerable winter temperature variability. A downward trend in the summer NAO between 1988 and 2012 was also associated with warming in Eastern Canada (Iles and Hegerl 2017). There is a moderate NAO effect on precipitation in Canada, and the effect is usually confined to the northeastern region. In this region, a positive NAO is generally related to reduced precipitation during winter (Bonsal and Shabbar 2011).

PDO was originally described by Zhang et al. (1997) and Mantua et al. (1997). PDO is a climate index that describes the variation in sea surface temperature in the North Pacific. The PDO phases shift on inter-decadal scales, usually every 20 to 30 years (Whitfield et al. 2010;

Bonsal and Shabbar 2011). During a positive PDO phase, the central and western Pacific sea surface becomes cooler and the west coast of North America (eastern portion) becomes warmer and vice versa (Mantua and Hare 2002). A strong association between the PDO and climate, hydrology and ecological processes have been reported (Pavia et al. 2006; Dong et al. 2016; Yang et al. 2017; Zhang et al. 2018; Wang et al. 2018a; Frazier et al. 2018). However, in Canada, PDO effects have only been observed in western regions (Mantua et al. 1997; Bonsal et al. 2001; Whitfield et al. 2010; Bonsal and Shabbar 2011). For example, winter temperature is generally higher than normal in western Canada during the positive phase of PDO (Bonsal et al. 2001; Whitfield et al. 2010).

1.4 Objectives

This study examined the long-term DOC patterns in lakes at four sites across eastern Canada with the following objectives:

- 1) characterize the patterns in DOC concentration at the four study sites in Eastern Canada over a 33 to 36-year period (i.e., ~1980-2015);
- 2) determine if these patterns were temporally coherent among lakes within a site and across sites;
- 3) examine the relationship between DOC and environmental variables (regional, global, or both) at each site; and
- (4) compare the results with past studies that examined long-term DOC patterns in eastern Canadian lakes (e.g., Zhang et al. 2010).

CHAPTER 2. DESCRIPTION OF STUDY SITES

2.1 Study sites

This study included 49 lakes from four sites across eastern Canada (Fig. 2.1). The study sites were Kejimikujik, Yarmouth, Dorset and the Experimental Lakes Area (ELA). Only lakes that had ≥ 33 years of DOC measurements were selected. Among the study sites, Kejimikujik and Yarmouth are in Nova Scotia, and Dorset and the ELA are in Ontario.



Figure 2.1. The location of the study sites across eastern Canada (modified from Zhang et al. 2010). Dorset and Experimental Lakes Area (ELA) sites are in Ontario. Kejimikujik and Yarmouth sites are adjacent to each other in Nova Scotia.

2.1.1 Kejimikujik and Yarmouth (Nova Scotia)

Twenty-seven lakes from the Kejimikujik site and eleven lakes from the Yarmouth site were included in the study. The Kejimikujik lakes are located in Kejimikujik National Park (KNP) of southwestern Nova Scotia (NS). The Yarmouth region is located near the Gulf of Maine in southwestern NS. The lakes are oligotrophic, polymictic, and show a wide range in size and

wetland coverage (Wyn et al. 2010). These sites consist of undisturbed catchments and are away from industrial and other point sources of pollution. Most of the areas are covered with fens or *Sphagnum* bogs (Clair and Sayer 1997). In general, the forest cover in KNP is representative of the Atlantic upland forest region (Rencz et al. 2003). It consists of a mixture of coniferous and deciduous vegetation. A wide variety of tree species can be abundant, but white spruce (*Picea glauca*), black spruce (*P. mariana*), white pine (*Pinus strobus*), eastern hemlock (*Tsuga canadensis*), white birch (*Betula papyrifera*) and red maple (*Acer rubrum*) are usually more common. The NS region has shallow soils and poor drainage conditions that have resulted in wet and boggy soils (Clair et al. 1996). It is underlain by two main rock sequences, the Meguma group of Cambro-Ordovician age and the South Mountain Batholith and related intrusive rocks of the Devonian-Carboniferous age (Rencz et al. 2003). This region primarily consists of stony till plain deposits that feature a loose texture, a sandy matrix and a large amount of stones and boulders. Acid buffering capacity in watershed soils typically depends on the quantity of base cations (e.g., Ca^{2+} , Mg^{2+} and so forth). The concentrations of base cations may vary based on the weathering of geological substances and on ion exchange reactions. Bedrock in NS watersheds is usually resistant to weathering, which has resulted in low concentrations of base cations in soils. As a result, NS watersheds have low acid-buffering capacity and can be sensitive to acidification (Clair et al. 1982; Kerekes et al. 1986). The concentrations of Ca^{2+} and Mg^{2+} in Kejimikujik were $38 \mu\text{Eq L}^{-1}$ and $39 \mu\text{Eq L}^{-1}$, respectively (McNicol et al. 1987). Also, past studies reported that NS watersheds have less buffering capacity than Ontario (Kelso et al. 1986). This makes NS the most sensitive to acidification among our study sites.

DOC concentrations ranged from 2.5 to 16.9 mg L^{-1} in Kejimikujik and 2.9 to 17.7 mg L^{-1} in Yarmouth (Fig. 2.2). The pH ranged from 4.3 to 6 in Kejimikujik and 4.8 to 6.6 in Yarmouth.

The surface area (A_o) of the study lakes ranged from 0.04 to 6.85 km² in Kejimikujik and from 0.15 to 1 km² in Yarmouth. The maximum depth (Z_{max}) ranged from 0.7 to 19.2 m in Kejimikujik and from 1.5 to 12.4 m in Yarmouth. The mean surface area to mean maximum depth ratio ($A_o : Z_{max}$) of 0.22 in Kejimikujik and 0.16 in Yarmouth indicate that the NS lakes are shallower than the other regions.

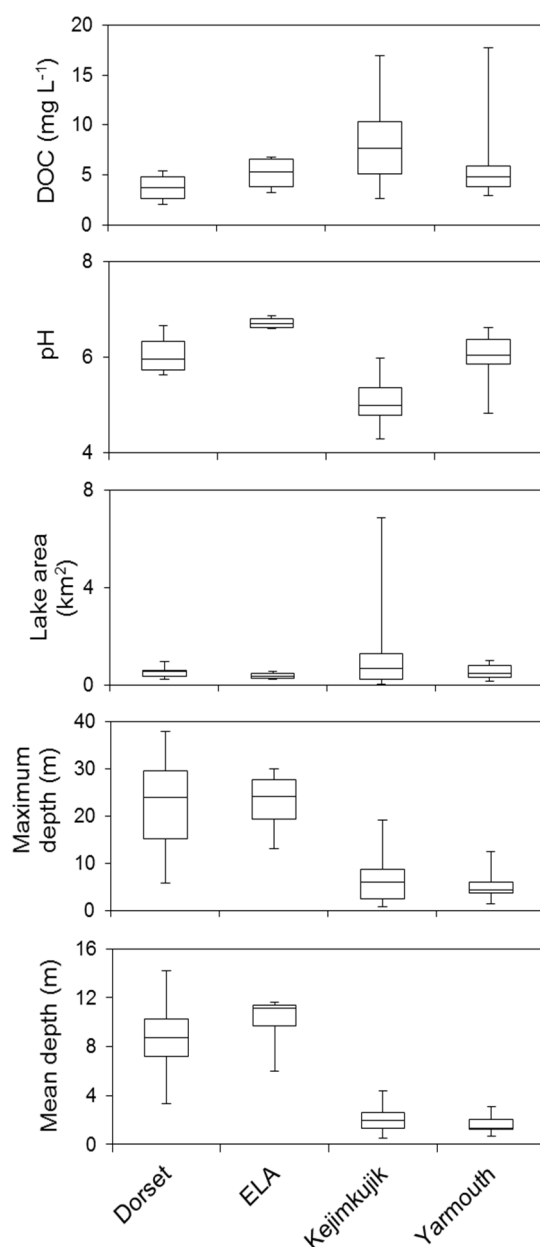


Figure 2.2. Summary of the chemical and physical properties of the lakes at each study site. Each boxplot consists of the maximum value, third quartile, median value, first quartile and minimum value.

2.1.2 Dorset

The eight Dorset study lakes are situated in the Muskoka District and Haliburton County region on the southern edge of the Precambrian Shield in south-central Ontario. In general, these are small, headwater dimictic lakes. The streams in this region are either first or second order. The catchments are predominantly forested with some cottage development (Dillon and Evans 2001). Some areas in the catchment had been cleared, but forests have been re-growing since early 1900s when farming ceased (Watmough and Dillon 2003). The upland forest areas are usually dominated by red oak (*Quercus rubra*), white pine (*P. strobus*), red maple (*A. rubrum*), sugar maple (*A. saccharum*), yellow birch (*B. alleghaniensis*) and eastern hemlock (*T. canadensis*). White cedar (*Thuja occidentalis*) and black spruce dominate in swamps (Watmough and Dillon 2004; O'Brien et al. 2013; Pinder et al. 2014). The catchments consist of Precambrian bedrock, generally granitized biotite and hornblende gneiss, with some areas consisting of amphibolite and schist (Molot and Dillon 2008). Peatlands range from 0 to 25% of the stream catchment areas. Generally, orthic humo-ferric, ferro-humic, sombric humo-ferric podzols and brunisols dominate in upland areas. Low-lying areas are usually dominated by cumulo-humisols and humic mesisols (Canadian Soil Survey Committee 1978). Some catchments have experienced disturbances to the vegetation. For example, a large number of deaths in trees has been associated with a water table increase. This increase was attributed to road construction in these areas in the mid-1970s (Pinder et al. 2014). Moreover, mixtures of salt and sand are used on roads in winter for better access. This has led to some road-salt contamination in some of the catchments (Watmough and Dillon 2003). The Dorset Environmental Science Center (DESC) meteorology station has been measuring major climate variables (e.g., precipitation, air pressure, solar radiation, humidity, air pressure) at this region since 1976 (Yao et al. 2018). Lake water

quality parameters have changed over the study period. For example, Ca and total phosphorus (TP) have decreased in most of the lakes (Watmough and Aherne 2008; Paterson et al. 2008), whereas pH has increased (Dillon et al. 2007; Yan et al. 2008). The bedrock of the Precambrian Shield region is very hard and resistant to weathering. Also, this region experiences low atmospheric deposition of base cations including Ca^{2+} (Watmough and Aherne 2008). This results in low concentrations of base cations in the Dorset watersheds. The concentrations of Ca^{2+} and Mg^{2+} in Dorset were reported to be $149 \mu\text{Eq L}^{-1}$ and $69 \mu\text{Eq L}^{-1}$, respectively (McNicol et al. 1987). Past studies have also reported an increase in loss of base cations in Dorset watersheds (Celis-Salgado et al. 2016; Watmough et al. 2016). Therefore, although the acid buffering capacity in the Dorset watersheds may be greater than NS and ELA (based on the concentrations of Ca^{2+} and Mg^{2+}), it is still sensitive to acidification (Reid and Watmough 2016).

The study lakes in Dorset are oligotrophic with low DOC concentration ($1.9\text{-}5.1 \text{ mg L}^{-1}$, Fig. 2.2). The pH ranged from 5.6 to 6.7. The surface area (A_o) of the lakes ranged between 0.21 and 0.94 km^2 . The maximum depth (Z_{max}) ranged from 5.8 to 38 m and the mean surface area to mean maximum depth ratio ($A_o : Z_{\text{max}}$) was 0.024.

2.1.3 Experimental Lakes Area (ELA)

Four unmanipulated reference lakes from the ELA were included in this study. These lakes are located on the Precambrian Shield of northwestern Ontario. The ELA is remote and away from most anthropogenic disturbances. The watersheds are undeveloped and only used occasionally for recreation. The ELA has a continental climate with warm summers, cold winters and short autumn and spring seasons (Heyes et al. 2000; Diodato et al. 2016; Mushet et al. 2018). The upland areas in the ELA are composed of lichen-covered Precambrian granite and shallow moss-covered soils ($< 0.05 \text{ m}$ thick). Watersheds in lowland areas generally consist of a large

coverage of wetland and peatland complexes (St Louis et al. 2004). In wetlands, open canopies are formed by black spruce (*P. mariana*) and tamarack (*Larix laricina*), and the *Sphagnum magellanicum* and *S. fallax* cover the hollows and lawns. Black spruce is found in shallow soils, while bryophyte mats, black spruce and jack pine (*P. banksiana*) cover the deeper soils (Heyes et al. 2000). The ELA lakes and watersheds are pristine and only affected by natural events. For example, three significant natural disturbances have occurred at the ELA during or before our period of study. A very strong windstorm along with an extreme thunderstorm hit the ELA region on July 7, 1973. Then, a severe forest fire burned a large area of the ELA on June 26, 1974 (Schindler et al. 1980). years later, on June 20, 1980, another forest fire burned the Lake 239 basin (Bailey et al. 1992a). Water and nutrient transport from the affected basin were significantly greater in subsequent years. Before the fire, uplands areas were covered by jack pine (*Pinus banksiana*), black spruce, paper birch (*B. papyrifera*), trembling aspen (*Populus tremuloides*), red pine (*P. resinosa*), white pine (*P. strobus*) and white spruce (*P. glauca*). After the fire, the affected areas revegetated quickly with small jack pine, black spruce, birch, balsam poplar (*Bopulus balsamifera*) and pin cherry (*Prunus pensylvanica*). The herbaceous and shrub vegetation were dominated by fireweed (*Epilobium angustifolium*), black bindweed (*Polygonum convolvulus*), blueberry (*Vaccinium spp.*) and raspberry (*Rubus strigosus*). However, after the second fire, revegetation was very slow (Bailey et al. 1992a). Similar to other Precambrian Shield watersheds, base cation concentrations in ELA watershed are low due to less weathering bedrock (Schindler et al. 1986; Jeziorski et al. 2014). The concentrations of Ca^{2+} and Mg^{2+} at the ELA were reported to be $98 \mu\text{Eq L}^{-1}$ and $49 \mu\text{Eq L}^{-1}$, respectively (McNicol et al. 1987). Moreover, a decline in Ca^{2+} at the ELA has been reported (Jeziorski et al. 2008; 2014). Therefore, ELA watersheds soils may have a reduced acid neutralizing capacity. Extensive

records of the characteristics of the study lakes and their catchments at the ELA have been documented elsewhere (see Brunskill and Schindler 1971; Schindler et al. 1980; Rudd et al. 1990; Bayley et al. 1992a; Bayley et al. 1992b; Schindler 1997; Heyes et al. 2000; Enache et al. 2011).

The ELA study lakes are oligotrophic and dimictic. Water columns are oxygenated throughout the year, and the vertical mixing in the water column occurs in spring and autumn (Diodato et al. 2016). DOC concentrations in the ELA lakes ranged from 3.1 to 6.7 mg L⁻¹ (Fig. 2.2). The pH ranged from 6.6 to 6.9. The surface area (A_o) of the lakes ranged between 0.26 and 0.54 km². The maximum depth (Z_{max}) ranged from 13 to 30 m and the mean surface area to mean maximum depth ratio ($A_o : Z_{max}$) was 0.017.

CHAPTER 3*: CHANGES IN THE LONG-TERM PATTERN OF DISSOLVED ORGANIC CARBON IN EASTERN CANADIAN LAKES AND ITS ASSOCIATION WITH REGIONAL AND GLOBAL FACTORS

3.1 Introduction

Increases in DOC concentration have been observed in freshwater systems during the last two decades across Europe (Monteith et al. 2007; Hruska et al. 2009; Erlandsson et al. 2011; Kopacek et al. 2015; Rodriguez-Murillo and Filella 2015; Oulehle et al. 2017; Sawicka et al. 2017) and North America (Driscoll et al. 2007; Monteith et al. 2007; Couture et al. 2012; Williamson et al. 2015; Singh et al. 2016; Strock et al. 2017; Jane et al. 2017; Brown et al. 2017). Such an increase in DOC can have multiple consequences. For example, it can alter the balance between algal photosynthesis and respiration (von Einem and Graneli 2010; Kritzberg et al. 2014; Kelly et al. 2014); restrict primary production by attenuating solar radiation (Jones et al. 2012; Godwin et al. 2014; Thrane et al. 2014; Seekell et al. 2015) and therefore, decrease the productivity of upper trophic levels including invertebrates and fish (Karlsson et al. 2009; Finstad et al. 2014; Kelly et al. 2014; Benoit et al. 2016). However, the effects of increasing DOC concentration on lake primary production are more complex. For example, nutrients bound with allochthonous DOC can stimulate primary production when released by photolysis (Klug 2002; Sereda et al. 2012; Kissman et al. 2013). Moreover, DOC can promote primary production by increasing dissolved CO₂ through photo-mineralization and bacterial mineralization, and by protecting phytoplankton from harmful UVR (Jansson et al. 2012; Lapierre et al. 2013). Because of DOC's binding capacity, increases in DOC could affect the mobility and toxicity of many metals including iron, aluminum and mercury (Lawlor and Tipping 2003; Clements et al. 2008; French et al. 2014; Braaten et al. 2018). The increase in light attenuation by rising DOC

**Chapter 3 has been prepared as a manuscript to submit for publication and may result in some repetitions with previous chapters. Authors are: Md Noim Imtiaz, Andrew Paterson, Huaxia Yao, Suzanne Couture, Scott Higgins and Jeff Hudson.*

concentration can result in an increase in reactive oxygen species (ROS) and free radicals (Dalrymple et al. 2010; Zhang et al., 2014; Krumova and Cosa 2016; Wolf et al. 2018) which can be detrimental to aquatic biota (Vehmaa et al. 2013; Wolf et al. 2017). Increased DOC concentrations can also pose a human health concern. Greater DOC concentrations can increase the treatment cost of surface waters that are used for drinking (Hongve et al. 2004; Ritson et al. 2014; Chowdhury 2018). DOC can also interact with chlorine during the treatment process and produce carcinogenic trihalomethanes (Chow et al. 2003; United States Environmental Protection Agency 2016; Chowdhury 2018).

Various hypotheses have been introduced to explain the increase in DOC in the Northern Hemisphere. The proposed factors associated with the DOC increase include regional factors such as precipitation, temperature and sulfate deposition (SO_4^{2-}). Among these, the reduction in sulfate deposition was identified as the most likely explanatory factor (De Wit et al. 2007; Monteith et al. 2007; Erlandsson et al. 2008; Dawson et al. 2009; Haaland et al. 2010; SanClements et al. 2012; Monteith et al. 2014). Sulfur oxide (SO_x) emission control programs were initiated in the 1980s as a result of the international concern over the acidification of natural waters and landscapes. Since the enactment of the American and Canadian clean air legislation, SO_4 deposition has declined significantly (Vet et al. 2005; Smith et al. 2011; Vet et al. 2014). It is proposed that a reduction in sulfate deposition caused an increase in pH levels and a decrease in ionic strength in soils. This, in turn, increased DOC solubility (Krug and Frink 1983; Monteith et al. 2007; Clark et al. 2010; Clark et al. 2011).

However, others have argued that long-term DOC patterns are mostly related to climate variables such as temperature, precipitation and solar radiation. Several studies have reported a strong positive relationship between DOC and rising air temperatures (Freeman et al. 2001;

Worrall and Burt 2007; Couture et al. 2012; Tian et al. 2013; Williams et al. 2016; Chow et al. 2017). Changes in climate can also influence the long-term patterns in precipitation. Precipitation can increase the DOC concentration in lakes by increasing its export from surrounding catchments (Correll et al. 2001; Raymond and Saiers 2010; Dyson et al. 2011; Yoon and Raymond 2012; Qiao et al. 2017). Precipitation has been found to be an important explanatory variable and included in many models to describe DOC dynamics (Hudson et al. 2003; Futter et al. 2007; Zhang et al. 2010; Couture et al. 2012; Diodato et al. 2016; Singh et al. 2016). In addition to temperature and precipitation, solar radiation has a long-term negative relationship with DOC and could decrease the DOC concentration by photochemical processes (Molot and Dillon 1997; Hudson et al. 2003; Molot et al. 2005; Sharpless and Blough 2014; Koehler et al. 2014; Mopper et al. 2015). Additionally, some global variables (i.e., Southern Oscillation Index, North Atlantic Oscillation, and Pacific Decadal Oscillation) were proposed to affect DOC concentration indirectly by influencing regional climatic variables such as temperature and precipitation (Dillon et al. 1997; Arvola et al. 2004, Bonsal and Shabbar 2011; Iles and Hegerl 2017). However, significant relationships between global variables and DOC concentration are uncommon in the literature.

Studies that have examined the long-term patterns in DOC in eastern Canada have provided different interpretations. For example, Monteith et al. (2007), Eimers et al. (2008) and Couture et al. (2012) reported an increase in DOC concentration in eastern Canada. Although Clair (2011) reported an increasing pattern between 2000 and 2007, this increasing pattern was not evident when a larger dataset was used (1990-2007). Furthermore, Hudson et al. (2003), Keller et al. (2008), and Zhang et al. (2010) did not find any evidence to support an increasing or decreasing DOC trend in most eastern Canadian lakes. Zhang et al. (2010) found an increasing

trend only in the Experimental Lakes Area (ELA) with a 21-year dataset. However, Diadato et al. (2016) reported a long-term cyclical pattern in DOC with a 40-year DOC record from the ELA. Similarly, different studies found different factors as the most important explanatory variables for the long-term patterns in DOC at these sites (e.g., see Monteith et al. 2007; Zhang et al. 2010; Couture et al. 2012; Diodato et al. 2016). Therefore, due to the lack of consistency in the literature, and the availability of longer DOC dataset, a re-examination of the long-term patterns in DOC and associated explanatory factors in eastern Canadian lakes was warranted. The main objectives of this study were to re-examine the patterns in DOC concentration in lakes from four sites in Eastern Canada over a 33 to 36-year period (i.e., ~1980-2015); to determine if these patterns are temporally coherent among lakes within a site and across sites; to identify the best explanatory variables associated with DOC (regional, global, or both); and to compare the new results with past studies in eastern Canadian lakes (e.g., Zhang et al. 2010).

3.2 Methods

3.2.1 Variables analyzed

Whole-lake ice-free DOC concentration (mg L^{-1}) was the dependent variable in this study. DOC measurements were completed 1-5 times per month from May to October in Dorset (1980-2015) and the ELA (1983-2015). At the ELA, DOC concentrations were measured individually for different thermal layers. To calculate the whole-lake DOC concentrations, we summed up the total DOC mass in each layer and divided by the lake volume. In Kejimikujik and Yarmouth, DOC concentrations were measured from 1983 to 2015 with 2 measurements per year, one at spring turnover (May) and a second at fall turnover (October). The detailed methods

for the measurement of DOC are found in Hudson et al. (2003) for Dorset; Stainton et al. (1977) for ELA; and Clair et al. (2008) for Kejimikujik and Yarmouth.

The long-term patterns in DOC at each site were examined as a function of seven explanatory variables. These included four regional variables: daily mean total solar radiation (TSR, KJ m^{-2}), monthly total precipitation (PPTN, mm), daily mean air temperature (T , $^{\circ}\text{C}$) and monthly total sulfate (SO_4) deposition (SD, mEq m^{-2}). The measurements of these explanatory variables were completed at the meteorological field stations at each site. In Kejimikujik and Yarmouth, TSR data was obtained from the nearby Kentville meteorological station which had data up to 1998. TSR data between 1999 and 2015 was obtained from the National Renewable Energy Laboratory (NREL) database (<https://nsrdb.nrel.gov/>). Moreover, SD data at the Yarmouth was not available. Hence, SD data that was available at the Kejimikujik was used for the Nova Scotia region (Zhang et al. 2010). At the ELA, only photosynthetically active radiation (PAR) was available. Therefore, TSR was calculated by dividing PAR by 0.457 (Rao 1984; Zhang et al. 2010). The rest of the explanatory variables were global variables that included the Southern Oscillation Index (SOI), Pacific Decadal Oscillation (PDO) and North Atlantic Oscillation (NAO). The data for global variables were obtained from the National Oceanic and Atmospheric Administration website (<http://www.cpc.ncep.noaa.gov/>). Each independent variable was examined in regard to long-term DOC pattern over various time periods: 1 month, 2 months, 3 months, 4 months, 5 months, 6 months, ice-free period (April-November) and annually within the year of DOC measurement and also from the past 5 years (lagged by 1-5 years) for a total of 139 temporal periods for each independent variable.

3.2.2 Statistical analyses

3.2.2.1 Temporal coherence in DOC patterns among lakes and sites

DOC concentration of each lake in all the study sites was standardized by Z-scoring in order to correct for the lake specific differences in DOC concentration. Temporal coherence in long-term DOC patterns among lakes within a site was analyzed using Pearson's correlation coefficient and Brien's test for correlation matrix homogeneity (Brien et al. 1984). If the long-term DOC patterns in lakes were temporally coherent within a site, then a single average DOC pattern was used to represent the variation in DOC for that site. Next, the temporal coherence in the average DOC patterns across sites was examined. Furthermore, the regional variables of different sites were analyzed to determine if they were synchronous across different sites. This analysis was done to determine if multiple sites could be pooled into a single site (e.g., see Zhang et al. 2010).

3.2.2.2 Relationship between DOC and explanatory variables

The relationship between the long-term DOC pattern and the independent variables listed above (regional and global) was examined at each site using multiple linear regression (MLR). To select the most parsimonious model(s) for each site, Akaike's Information Criteria (AIC) was used because it was considered superior to conventional model selection methods (Anderson et al. 2000). Due to the enormous number of models to be tested at each site (7^{139}), the number of variables (time periods) needed to be reduced. At first, we examined the correlation between DOC and each set of explanatory variables for all 139 time periods. Then, we retained the time periods that were significantly correlated with DOC ($p < 0.05$). The separate MLR analyses were run on these retained time periods of each explanatory variable (Hudson et al. 2003). The

significant time periods from the separate MLR analyses were then identified and retained for the final MLR analyses that included all the significant time periods of each independent variable. To select the best model and competing models, we calculated the AIC_c value for every combination of significant variables for each site. AIC_c is the second order AIC which is considered more appropriate when the ratio of sample size (n) to the number of independent variables (k) is small (i.e., $n : k < \sim 40$; Anderson et al. 2000; Burnham and Anderson 2002). The relative goodness of fit of each model in each site was examined by progressively calculating Akaike's weight (w_i) and the evidence ratio (ER) from the AIC_c value. The ER of the best model was 1 and any models with $1 < ER < 2.7$ were considered competing models (Burnham et al. 2011). Only the best model and competing models (if any) at each study site are described here.

3.3 Results

3.3.1 Differences in study sites

The lowest mean DOC concentration was observed in the Dorset lakes (3.7 mg L^{-1} , C.V. = 10.9%, Table 3.1). The average DOC concentration in four ELA lakes was 4.9 mg L^{-1} (C.V. = 6.9%). The Kejimikujik and Yarmouth lakes had greater average DOC concentration than Dorset and ELA lakes. DOC concentrations in Kejimikujik and Yarmouth were 7.9 and 6.3 mg L^{-1} , respectively. Furthermore, the Kejimikujik and Yarmouth lakes had greater variability in DOC concentration than other sites (C.V. = 22.6% and 21.0%, respectively). The Kejimikujik and Yarmouth lakes were also the most acidic while ELA lakes were the least acidic (Fig. 2.2).

The ELA site experienced the lowest amount of precipitation (Table 3.1). Precipitation and total solar radiation were greatest in NS and Dorset, respectively. The NS region had the

highest mean annual temperature and the ELA had the lowest. The ELA site received the least amount of annual total SO₄ deposition.

Table 3.1. Summary of mean ice-free DOC concentration (mg L⁻¹), daily total solar radiation (TSR, annual mean, kJ m⁻²), monthly precipitation (PPTN, total from May to October, and annual total, mm), daily air temperature (T, annual mean, °C) and monthly SO₄ deposition (SD, annual total, mEq m⁻² year⁻¹) of all the study sites. The coefficients of variation (C.V. %) are presented in parentheses. Data extend from 1983 to 2015 at all sites, except for Dorset, where data extend from 1980 to 2015.

Variable	Dorset	ELA	Kejimkujik	Yarmouth	NS*
Mean ice-free DOC	3.7 (10.9)	4.9 (6.9)	7.9 (22.6)	6.3 (21.0)	7.1 (21.4)
TSR (Annual mean)	15908.1 (6.6)	15112.84 (9.4)	12567.7 (4.5)	12615.8 (4.5)	12591.7 (4.5)
PPTN (May-Oct)	534.0 (18.2)	514.1 (21.2)	622.2 (22.3)	576.1 (22.6)	599.1 (21.2)
PPTN (Annual total)	1010.2 (13.0)	708.9 (18.5)	1447.4 (16.4)	1302.4 (13.5)	1374.3 (12.8)
T (Annual mean)	5.1 (16.3)	3.0 (37.1)	6.9 (12.6)	7.2 (9.2)	7.1 (10.5)
SD (Annual total)	41.9 (36.1)	15.8 (30.5)	22.3 (32.9)	-	22.3 (32.9)

* Combined mean of Kejimkujik and Yarmouth sites

3.3.2 Temporal coherence in long-term trends in DOC and regional variables

The long-term DOC pattern at Beaverskin lake did not show a synchronous pattern with the other 26 lakes at the Kejimkujik site. Therefore, Beaverskin was excluded from any further analysis. The long-term DOC patterns of all lakes within a site were temporally coherent over the study period (Pearson's correlation coefficient, $p < 0.05$; Brien's test, $p > 0.05$, Fig. 3.1A, Table

3.2). Thus, all the lakes within a site were combined into a single average DOC pattern, and this mean DOC pattern was used to represent the long-term DOC pattern of each site (Fig. 3.1B).

A second temporal coherence analysis across sites showed that the long-term DOC patterns between Kejimikujik and Yarmouth had the strongest correlation ($r = 0.86$, $p < 0.001$, Table 3.3). Long-term patterns in temperature and SO_4 deposition were synchronous across all the study sites. However, long-term trends in total solar radiation and precipitation were not synchronous across the regions, except between Kejimikujik and Yarmouth. DOC and all the regional variables were temporally coherent only between Kejimikujik and Yarmouth (Table 3.3). Therefore, we could not combine other sites into a single site because all the variables did not show synchronous patterns across sites. Only Kejimikujik and Yarmouth were pooled into a single Nova Scotia (NS) site (Fig. 3.1). As a result, the initial number of study sites (four) was reduced to three sites: Dorset, ELA and NS. A single mean long-term DOC pattern for each study site was used in later analyses.

Table 3.2. Temporal coherence of the long-term DOC patterns in lakes within a site. Long-term patterns in DOC were synchronous within a site. However, Beaverskin was not correlated with the other 26 lakes in Kejimikujik ($0.01 \leq r \leq 0.37$) and was eliminated from further analyses.

Site	No. of Lakes	Pearson's correlation coefficient (r)	
		Mean	Range
Dorset	8	0.76	0.51-0.91
ELA	4	0.75	0.66-0.83
Kejimikujik	26	0.77	0.48-0.96
Yarmouth	11	0.76	0.44-0.92

Table 3.3. Temporal coherence of the long-term patterns in DOC and the regional variables across study sites. Long-term patterns in DOC and all regional variables were only temporally coherent between Kejimikujik and Yarmouth.

Variable	Study site	Pearson's correlation coefficient (r)		
		Dorset	ELA	Kejimikujik
DOC	ELA	0.64**	1	
	Kejimikujik	0.41*	0.29	1
	Yarmouth	0.51*	0.30	0.86**
TSR	ELA	-0.09	1	
	Kejimikujik	-0.20	-0.30	1
	Yarmouth	-0.09	-0.30	0.95**
PPTN	ELA	0.03	1	
	Kejimikujik	0.17	0.08	1
	Yarmouth	0.14	0.11	0.56**
T	ELA	0.84**	1	
	Kejimikujik	0.72**	0.56**	1
	Yarmouth	0.72**	0.57**	0.85**
SD	ELA	0.70**	1	
	Kejimikujik	0.83**	0.64**	1

** Correlation is significant at 0.01 level of significance

* Correlation is significant at 0.05 level of significance

3.3.3 Long-term patterns in DOC and regional variables

Evidence to support an increasing or decreasing trend in Dorset between 1980 and 1997 was not present (Fig. 3.1B). However, an increase in DOC concentration in Dorset lakes was evident between 1997 and 2015 (increase of $0.12 \text{ mg L}^{-1} \text{ year}^{-1}$, $r^2 = 0.68$, $p < 0.001$). Likewise, increases in DOC concentration were also apparent between 2000 and 2015 in Kejimikujik lakes (increase of $0.12 \text{ mg L}^{-1} \text{ year}^{-1}$, $r^2 = 0.42$, $p = 0.007$, Fig. 3.1B), and in Yarmouth lakes (increase of $0.11 \text{ mg L}^{-1} \text{ year}^{-1}$, $r^2 = 0.30$, $p = 0.03$, Fig. 3.1B). The combined site, NS also showed a similar increase in DOC in the last two decades (increase of $0.11 \text{ mg L}^{-1} \text{ year}^{-1}$, $r^2 = 0.34$, $p = 0.02$, Fig. 3.1B). There was an increasing trend in the ELA between 1983 and 2000 (increase of $0.10 \text{ mg L}^{-1} \text{ year}^{-1}$, $r^2 = 0.39$, $p = 0.005$, Fig. 3.1B). However, this increase was not evident in the ELA in last two decades.

The long-term pattern in annual total precipitation showed an increasing trend in the ELA ($r^2 = 0.13$, $p = 0.03$, Fig. 3.2A) and NS ($r^2 = 0.33$, $p < 0.001$, Fig. 3.3A). TSR decreased in the ELA ($r^2 = 0.18$, $p = 0.01$, Fig. 3.2B), but slightly increased in NS ($r^2 = 0.12$, $p = 0.04$, Fig. 3.3B). Long-term patterns in temperature showed a significant rising trend in NS ($r^2 = 0.25$, $p < 0.01$, Fig. 3.3C) and Dorset ($r^2 = 0.12$, $p = 0.04$, Fig. 3.4A). On the other hand, annual SO_4 deposition declined significantly in all the study sites ($0.41 < r^2 < 0.89$, $p < 0.001$, Fig. 3.2-3.4).

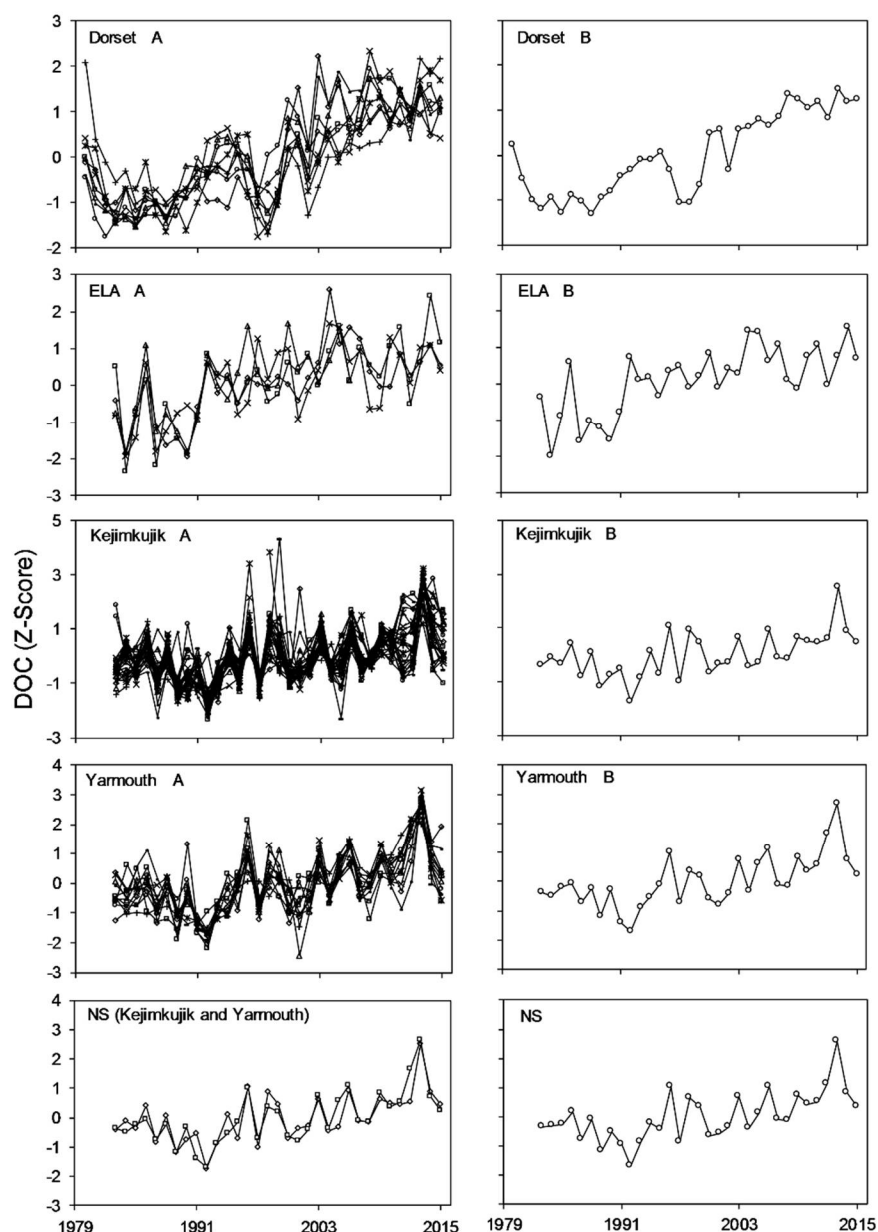


Figure 3.1. Long-term DOC patterns in the lakes that were found to be temporally coherent within a site (A). The number of temporally coherent lakes in Dorset, ELA, Kejimikujik and Yarmouth were 8, 4, 26 and 11, respectively. DOC patterns in all the temporally coherent lakes within a site were combined into a single pattern to represent the long-term DOC pattern for a site (B). DOC patterns across sites were only temporally coherent between Kejimikujik and Yarmouth. Therefore, Kejimikujik and Yarmouth were pooled into a single Nova Scotia (NS) site. DOC concentrations were standardized by Z-scoring in order to correct for lake specific differences in DOC concentration.

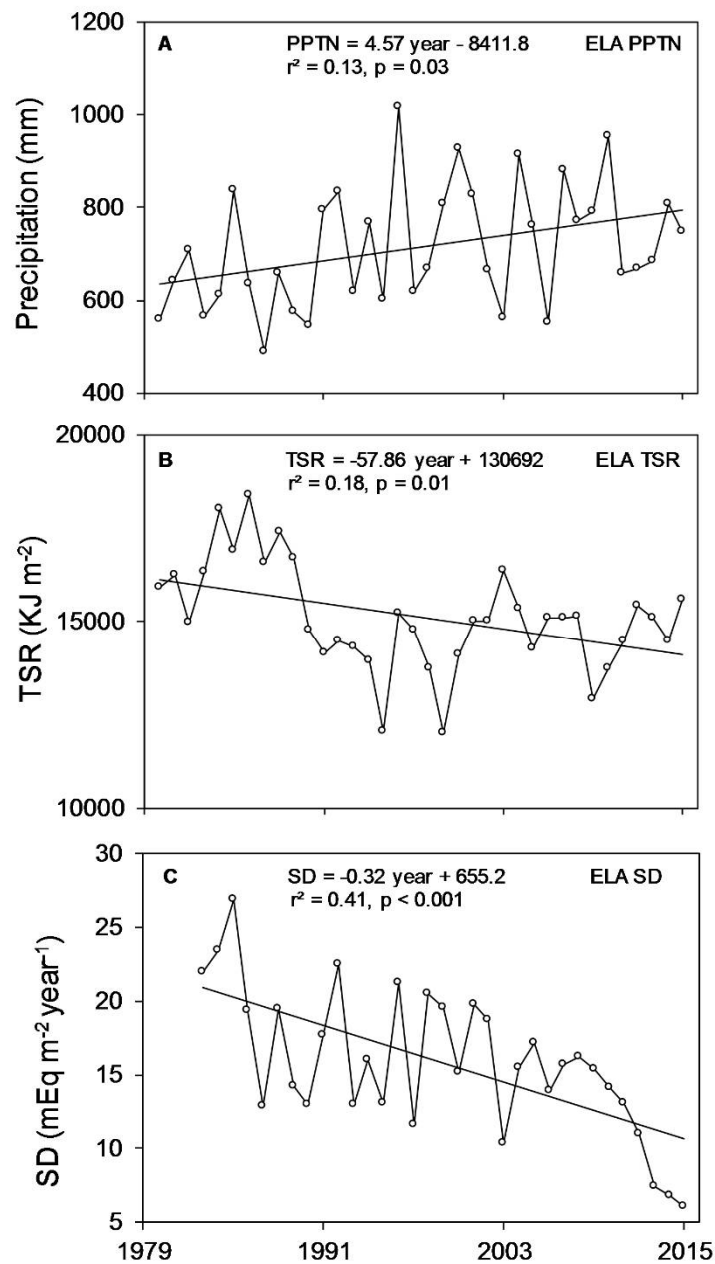


Figure 3.2. Long-term patterns in variables that were found to be significantly increasing or decreasing over the study period at the ELA. Annual total precipitation showed a significant increase (A). However, annual mean total solar radiation (B) and, annual total SO₄ deposition showed a significant decrease (C).

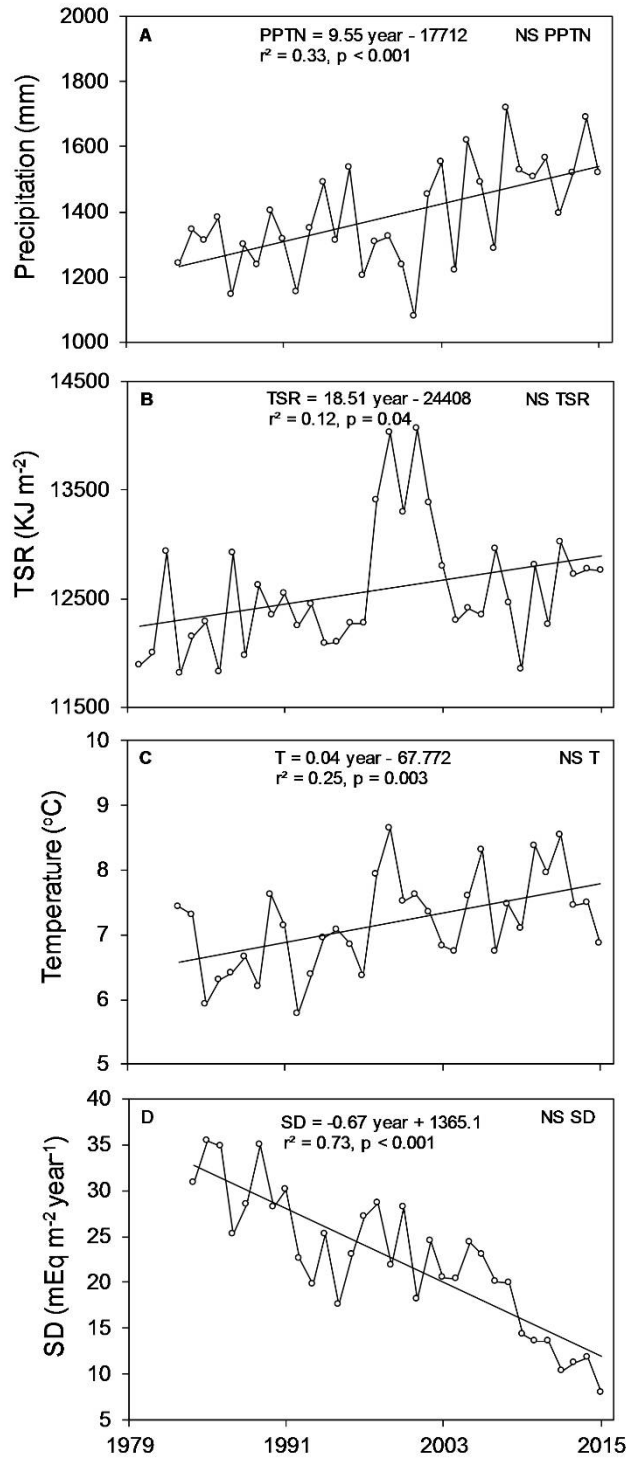


Figure 3.3. Long-term patterns in variables that were found to be significantly increasing or decreasing over the study period at the Nova Scotia (NS). Annual total precipitation (A), annual mean total solar radiation (B) and annual mean temperature showed a significant increase (C). However, annual total SO₄ deposition showed a significant decrease (D).

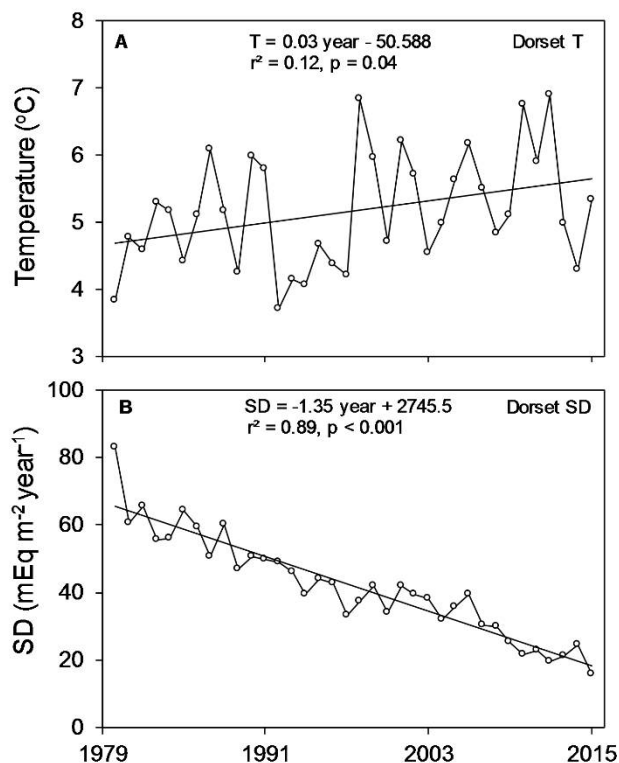


Figure 3.4. Long-term patterns in variables that were found to be significantly increasing or decreasing over the study period at the Dorset. Annual mean temperature showed a significant increase (A). However, annual total SO₄ deposition showed a significant decrease (B).

3.3.4 Relationship of DOC pattern with regional and global variables

3.3.4.1 Dorset

Two possible models were selected for the Dorset region (Table 3.4). The best model had three independent variables and explained 75% of the total variation in the long-term pattern in DOC. The selected variables were sulfate deposition (annual total), NAO (July-August) and PDO (1-year lag). These variables had a negative relationship with DOC (Fig. 3.5A, 3.5C-D). In the competing model, NAO was replaced by summer precipitation (June-August) which had a positive relationship with DOC (Fig. 3.5B). The competing model increased the explained variation to 80% from 75% in the best model.

3.3.4.2 Nova Scotia (NS)

A single model was selected to explain the long-term pattern in DOC in NS. This model contained four explanatory variables that explained 88% of the variation in the long-term DOC pattern (Table 3.4). Among the four selected variables, summer precipitation (June-October) and summer temperature (July) had a positive relationship with DOC (Fig. 3.6A, 3.6C). On the other hand, winter sulfate deposition (previous year's October-February) and NAO (Previous year's April-Previous year's November) had a negative relationship with DOC (Fig. 3.6B, 3.6D).

3.3.4.3 Experimental Lakes Area (ELA)

A single model was selected for the ELA (Table 3.4). The model had three independent variables and it explained 47% of the variation in the long-term pattern in DOC. The selected independent variables, sulfate deposition (Previous year's June-Previous year's August), sulfate deposition (December) and temperature (April-August) had a negative relationship with DOC (Fig. 3.7A-C).

Table 3.4. Summary of the relationships between DOC and regional and global variables at each study site. The models were developed using MLR, and the most parsimonious model(s) were selected using AIC. Only the best model (ER = 1) and the competing models ($1 < \text{ER} < 2.7$) at each site were selected and shown here. The most common explanatory variable to describe the long-term pattern in DOC at all sites was SO_4 deposition. Global variables were another important set of explanatory variables in Dorset and NS.

Region	Model	Explanatory Variable	Coefficient	Variance Explained (%)	R^2	w_i	ER
Dorset	1	SD (Annual Total)	-0.03	41	0.75***	0.32	1.00
		NAO (Jul-Aug)	-0.42	24			
		PDO (1-year lag)	-0.37	10			
	2	SD (Annual Total)	-0.04	45	0.80***	0.18	1.80
		PPTN (Jun-Aug)	0.01	27			
		PDO (1-year lag)	-0.28	8			
NS	1	PPTN (Jun-Oct)	0.004	55	0.88***	0.39	1.00
		SD (Prev. Oct-Feb)	-0.12	14			
		T (Jul)	0.20	10			
		NAO (Prev. Apr-Prev. Nov)	-0.47	9			
ELA	1	SD (Prev. Jun-Prev. Aug)	-0.17	21	0.47***	0.12	1.00
		SD (Dec)	-0.93	20			
		T (Apr-Aug)	-0.15	6			

*** Significant at $p < 0.001$ level

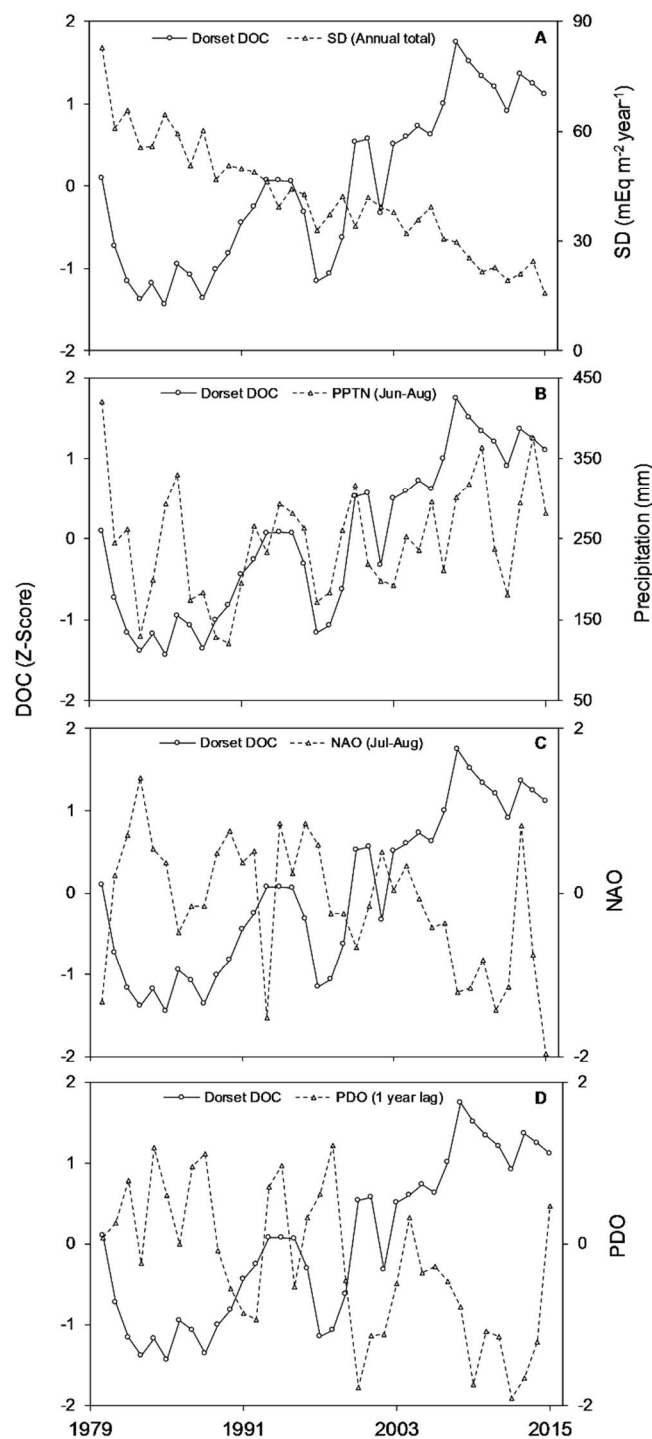


Figure 3.5. The relationship between the selected explanatory variables and the long-term pattern in DOC at Dorset. SO_4 deposition (SD, annual total) (A), North Atlantic Oscillation (NAO, July to August) (C) and Pacific Decadal Oscillation (PDO, 1-year lag) were negatively correlated with DOC (D). However, summer precipitation (PPTN, June to August) had a positive relationship with DOC (B).

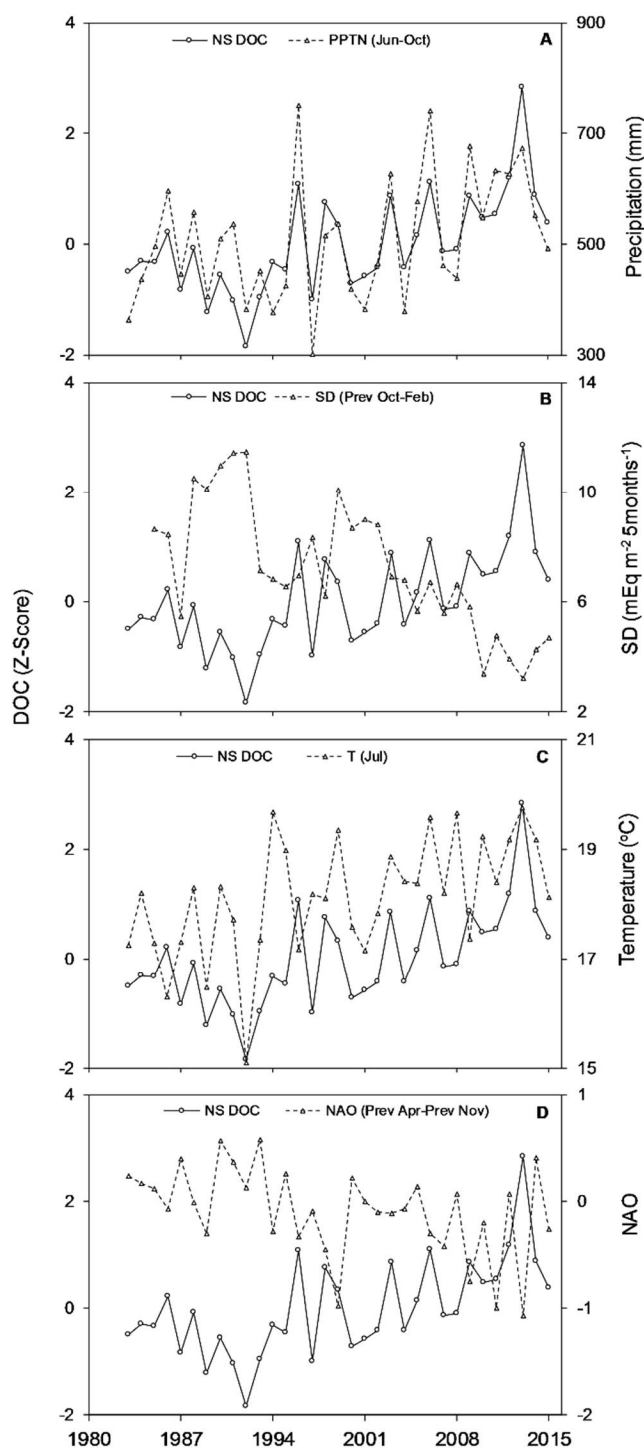


Figure 3.6. The relationship between the selected explanatory variables and the long-term pattern in DOC at NS. Summer precipitation (PPTN, June to October) (A), summer temperature (T, July) were positively correlated with DOC (C). However, SO_4 deposition (SD, previous year's October to February) (B) and North Atlantic Oscillation (NAO, previous year's April to previous year's November) had a negative relationship with DOC (D).

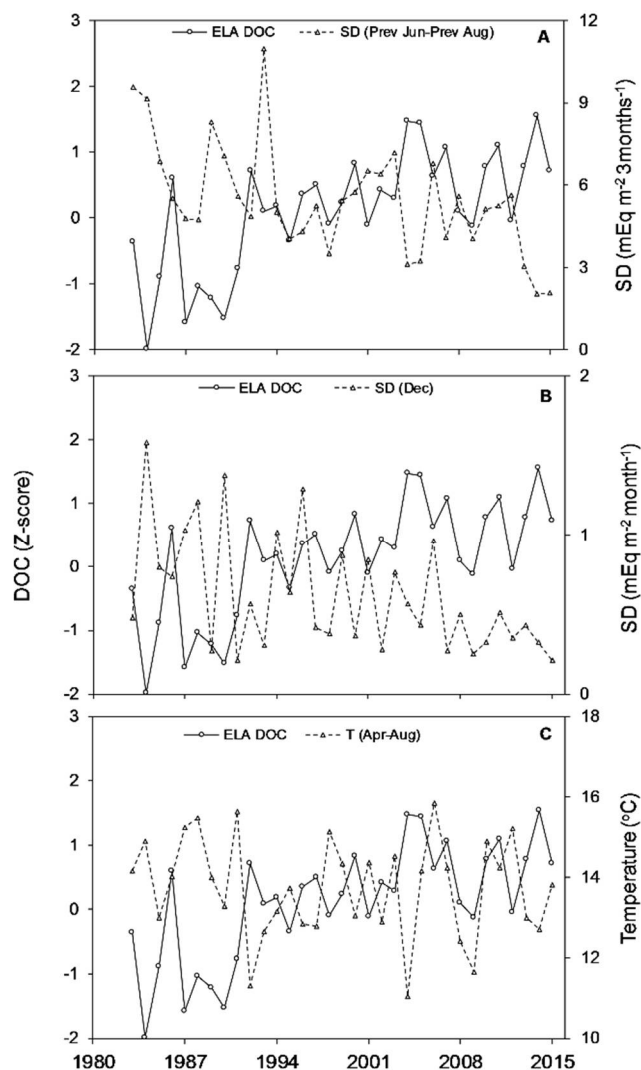


Figure 3.7. The relationship between the selected explanatory variables and the long-term pattern in DOC at the ELA. SO₄ deposition (SD, Previous year's June to previous year's August) (A), SD (December) (B) and summer temperature (T, April to August) were negatively correlated with DOC (C).

3.4 Discussion

3.4.1 Differences in DOC concentrations among sites

Differences in ice-free DOC concentrations in our study sites may be associated with differences in local and regional factors among the sites. For example, DOC concentration was

significantly greater in the NS sites than the Ontario sites (Dorset and ELA) (Table 3.1, Fig. 2.2). Greater concentrations of DOC have been attributed to a greater proportion of wetlands in the catchment of lakes (Dillon and Molot 1997; Richardson et al. 2010; Hosen et al. 2018). The NS sites consist of a greater proportion of wetlands in their catchments compared to other sites (Clair et al. 1994), which may contribute to the greater DOC concentration in NS. Different climate characteristics may also explain the variation in DOC concentrations. NS sites encounter significantly higher annual total precipitation and annual mean temperature than other sites (Table 3.1). The positive effects of precipitation and temperature on DOC concentration are well explained. Higher precipitation can significantly increase the DOC concentration in lakes by increasing the export of allochthonous DOC from the terrestrial environment (McClain et al. 2003; Raymond and Saiers 2010; Dyson et al. 2011; Yoon and Raymond 2012; Qiao et al. 2017). Precipitation can also increase the DOC concentration through wet deposition of DOC (Safieddine and Heald 2017). Moreover, higher temperatures can increase the DOC concentration by increasing decomposition rates (Freeman et al. 2001).

3.4.2 Temporally coherent patterns in DOC and regional variables

We observed temporally coherent DOC patterns in lakes within a site (Fig. 3.1A). However, across sites, we only observed temporally coherent DOC patterns between Kejimikujik and Yarmouth (Table 3.3). Kejimikujik and Yarmouth are located only 80 km apart from each other (Fig. 2.1) and hence, DOC and the regional variables would be more prone to being temporally coherent between these sites than the other sites which are much further apart (Koenig 2002; Anderson et al. 2018). For example, except for NS sites, regional climate variables like precipitation and solar radiation were not temporally coherent across the sites (Table 3.3). These variables vary considerably across regions which may also depict the large

distance and difference in climate types among the sites. The NS site has a coastal climate, whereas the ELA and Dorset sites experience more of a continental climate. On the other hand, long-term patterns in temperature and SO₄ deposition were the only variables that were temporally coherent across all the sites (Table 3.3). An increase in temperature over a longer study period in the Ontario and NS sites has already been reported (Keller et al. 2008; Ruhland et al. 2010; Ginn et al. 2008; Korosi et al. 2013). Although temperature showed an upward trend in these three regions, the annual mean temperature was still greater in the coastal areas (i.e., NS, Table 3.1). Despite a synchronous declining pattern in SO₄ deposition across sites, annual total SO₄ deposition showed considerable variability across sites (Table 3.1). Also, the effects of declining SO₄ deposition on different watersheds should vary as a result of the variation in the concentrations of base cations and soil acid buffering capacity among the sites (see section 2.1.1-2.1.3). For example, NS site has the lowest acid buffering capacity among the sites. This could be associated with the slowest recovery from acidification in NS watersheds. Therefore, a significant increase in pH was not evident in NS until early 2000s (Fig. 3.8), despite a decline in SO₄ deposition (Fig.3.3).

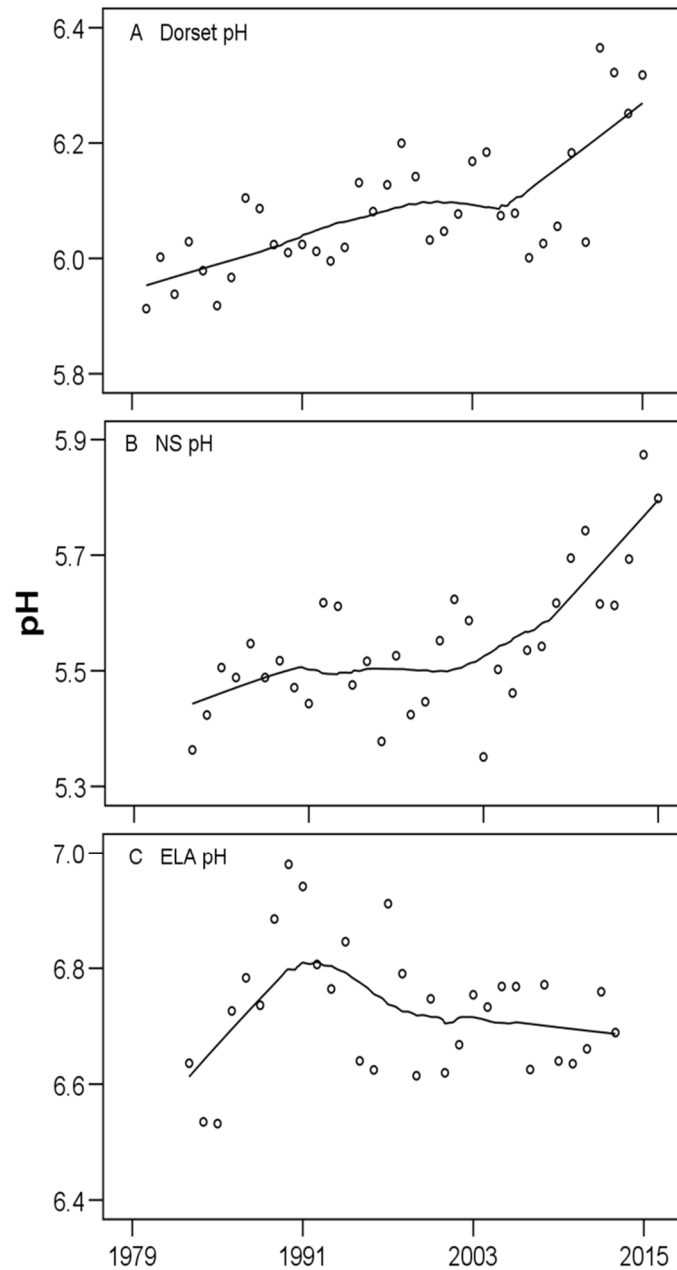


Figure 3.8. Long-term trends in lake pH at the study sites. A LOESS smoothed line was fitted to the observations at each site. There was an increase in pH at Dorset (A) and at Nova Scotia (B) in the last two decades. However, an increase or decrease in pH was not apparent at the ELA in the last two decades (C).

3.4.3 Long-term patterns in DOC

Long-term trends in DOC at the study sites have undergone significant changes since the study of Zhang et al. (2010). In addition, the long-term DOC pattern at the ELA study lakes has changed in a unique manner from that of the Dorset and NS site lakes. Therefore, the DOC pattern in the ELA will be discussed separately later. Zhang et al. (2010) reported a cyclic pattern in DOC at Dorset and NS and suggested that additional years of data were required to determine if the cyclic patterns would continue after the years of their study. With an additional ~15-year dataset, we observed that the cyclic pattern did not continue in Dorset and NS. Rather, significant increases in DOC were evident in last two decades in Dorset and NS (Fig. 3.1). As mentioned earlier, such increases in DOC concentration in the Northern Hemisphere are well documented. These increases in DOC concentration have mostly been attributed to the process of recovery from acidification due to the decline in SO_4 deposition (Evans et al. 2006; Monteith et al. 2007; Dawson et al. 2009; Haaland et al. 2010; SanClements et al. 2012; Monteith et al. 2014). A consistent decline in SO_4 deposition was also evident in our study sites (Fig. 3.2-3.4) and it has explained a significant amount of variation in the long-term patterns in DOC (Table 3.4).

However, Dorset and NS sites showed a delayed response in the increase in DOC when compared to other regions in Europe and North America. For example, the U.K. Acid Waters Monitoring Network (AWMN) experienced an increase in DOC starting in 1988 (Evans et al. 2005). Hejzlar et al. (2003) reported an increase in DOC in the Czech Republic since the mid-1980s. Forsius et al. (2003) found increasing DOC in a large Finnish lake dataset in the 1990s. Stoddard et al. (2003) observed a significant increase in DOC from 1990 in northern and eastern U.S. Increases in DOC were also reported in the Adirondacks, New York, since 1982 (Driscoll et al. 2003) and in southern Quebec since 1985 (Bouchard 1997). In Dorset and NS, the SO_4

deposition started to decline in advance of the increases in DOC (Fig. 3.5A, 3.6B), particularly in Dorset lakes. The recovery from acidification could be delayed due to the release and oxidation of internal sulfur in catchments that were previously stored in soil during high SO_4 deposition years (Dillon et al. 1997, Watmough et al. 2005; Mitchell et al. 2011; Garmo et al. 2014). Moreover, as mentioned earlier, watersheds in Dorset and NS have lower acid buffering capacity because concentrations of base cations are lower in watershed soils (see section 2.1.1 and 2.1.2). Low acid buffering capacity typically makes watersheds sensitive to acidification and may delay the recovery process. As a result, changes in SO_4 deposition could take decades to significantly affect the DOC concentration in lakes.

Among our study sites, Zhang et al. (2010) found an increasing DOC trend only in the ELA study lakes starting from 1990 (Fig. 3.1). This earlier recovery in the ELA may be explained by different amounts of SO_4 deposition at different sites. The total amount of SO_4 deposition per year at the ELA was lower than in Dorset and NS (Table 3.1). Thus, the amount of previously stored sulfur in the ELA watersheds was likely lower than in other two sites. Also, less amount of internal sulfur was likely to be released and oxidized in subsequent years in the ELA watersheds. Therefore, declining SO_4 deposition may have affected the DOC concentration much earlier at the ELA and contributed to an earlier increase in DOC.

3.4.4 General relationships between DOC and the regional explanatory variables

There have been significant changes in the variables that best explained the pattern in DOC at our study sites since the Zhang et al. (2010) study. Although Zhang et al. mentioned that a declining SO_4 deposition effect could be present in their 21-year dataset, SO_4 deposition was not selected in any of their best or competing models. This is likely a result of the absence of an increasing DOC pattern (except for ELA) at the study sites prior to the late 1990s. In addition,

SO₄ deposition was not selected in the best models presumably because of the counteracting effect of the release of previously stored sulfur from soils (as mentioned earlier). Furthermore, although sulfur emission control programs were initiated in early 1980s, implementation in Canada was only achieved by 1994 (Environment Canada 1996; Environment and Climate Change Canada 2017). Therefore, a considerable portion of the 21-year dataset of Zhang et al. (2010) included years before the sulfur emission control programs were fully implemented. With the additional 15 years of study presented here, SO₄ deposition was selected in all the best and competing models (Table 3.4). As the SO₄ deposition declined over the study period, an increase in lake pH was observed at Dorset and NS sites (Fig. 3.8A-B). However, this relationship was not evident at the ELA (Fig. 3.8C), and an explanation for this will be discussed later.

Reduction in SO₄ deposition is expected to increase lake DOC concentration by increasing the mobility of DOC from less acidic watersheds (Evans et al. 2005; Monteith et al. 2007). Reduced acidity may increase DOC concentration primarily by increasing soil pH, and secondarily by decreasing the mobilization of aluminum that may bind with DOC (Monteith et al. 2007). Moreover, reduced acidic deposition may result in reduced multivalent ions (e.g., SO₄²⁻, Ca²⁺, Mg²⁺) which can reduce the ionic strength in soil (De Wit et al. 2007; Monteith et al. 2007; Hruska et al. 2009). This reduction in ionic strength increases the surface charge and electrostatic repulsion of C-DOC and hence, reduces flocculation, coagulation and precipitation of C-DOC (Tipping and Hurley 1988; Haaland et al. 2010). As a result, a decline in ionic strength should increase the export of allochthonous DOC from soils (Evans et al. 1988). Furthermore, declining SO₄ deposition should lead to an increase in lake pH (as seen at Dorset and NS site, Fig. 3.8A-B), and in turn, a reduction in acid-enhanced in-lake photodecomposition of DOC (Gennings et al. 2001; Kohler et al. 2002; Molot et al. 2005).

Precipitation was another regional variable that explained a significant amount of variation in the long-term patterns in DOC at Dorset and NS. Because there is a very strong relationship between DOC export and runoff (Dillon and Molot 2005), an increase in precipitation can induce a significant loss from the terrestrial organic carbon pool and thus, increase the DOC export from terrestrial to aquatic systems (McClain et al. 2003; Raymond and Saiers 2010; Dyson et al. 2011; Yoon and Raymond 2012; Qiao et al. 2017). A strong positive relationship between DOC and precipitation was observed during the summer (i.e., May to October). Such a relationship between DOC and precipitation was also observed by Zhang et al. (2010) in Dorset and NS. Other studies also reported a significant increase in DOC concentration in streams and lakes with forested catchments when summer precipitation increased (Easthouse et al. 1992; Hinton et al. 1997; Kohler et al. 2008), especially when labile DOC is produced from the oxidation of the upper layer of peat in watersheds (Dillon and Molot 1997; Freeman et al. 2001; Eimers et al. 2008). Moreover, DOC concentration in lakes can also increase through the wet deposition of DOC in precipitation (Safieddine and Heald 2017). DOC concentration in precipitation has been reported to range between 0.2 mg L⁻¹ and 11.4 mg L⁻¹ (Iavorovska et al. 2016).

However, an increase in precipitation can also have a reverse effect on DOC concentration. Heavy precipitation events can dilute lake DOC concentrations. This has been observed when heavy precipitation events occur in early spring when DOC is still limited in the frozen soils and peats (Schiff et al. 1998; Hudson et al. 2003). This scenario might result in a negative relationship between DOC concentration and winter, or early spring precipitation. Such a dilution effect of heavy precipitation on DOC has also been reported to cause low DOC

concentrations elsewhere (Li et al. 2016). However, we did not observe any negative relationships between DOC and precipitation in our current longer-term study.

In the best models for NS and the ELA, temperature was selected as one of the most important explanatory variables (Table 3.4). In NS, there was a positive relationship between DOC and temperature (Fig. 3.6B). Such a positive relationship has also been observed elsewhere (Freeman et al. 2001; Keller et al. 2008; Worrall and Burt 2007; Couture et al. 2012; Tian et al. 2013). An increase in temperature may increase the DOC concentration by several mechanisms. For example, rising temperature can increase DOC concentration in peat soils by increasing decomposition rates via microbial processes (Freeman et al. 2001). This increase in peat soil DOC can subsequently increase DOC concentration in water.

However, the positive relationship between DOC and temperature is not ubiquitous and we also observed a negative relationship at the ELA site (Table 3.4, Fig. 3.7B). This negative relationship between DOC and temperature was reported earlier by Schindler (1997) at the ELA. The decline in flow that is associated with rising temperature could result in a reduced export of DOC from catchments (Schindler et al. 1996), and subsequently, a decline in DOC concentrations in lakes (Schindler 1997). Bertolet et al. (2018) also reported that warmer and drier conditions can result in a decline in terrestrial DOC inputs to lakes and cause a decrease in DOC concentration. Furthermore, warmer condition can increase water retention time in lakes by decreasing flow and increasing evaporation. This could increase the exposure of DOC to microbial and photochemical mineralization processes and consequently, reduce DOC concentration (Schindler et al. 1996). Shirokova et al. (2013) reported a similar association between temperature and DOC. They found that DOC concentration in a humic boreal lake decreased by more than 30% during an unusually hot summer. They attributed the decrease in

DOC to an increased rate of mineralization by heterotrophic bacterioplankton, and an increased rate of photodegradation. However, we only observed a weak negative relationship between DOC and temperature at the ELA (i.e., temperature explained only 6% of total variation in DOC, Table 3.4).

In their 21-year dataset, Zhang et al. (2010) reported that solar radiation was one of the most important explanatory variables affecting the DOC pattern at our study sites. The negative short and long-term effects of total solar radiation have been well explained by previous studies (Kopacek et al. 2003; Hudson et al. 2003; Shiller et al. 2006; Zhang et al. 2010; Porcal et al. 2013). With additional data, however, total solar radiation was not selected in any of the parsimonious models for the study sites in the present study (Table 3.4). An increase or decrease in total solar radiation was not present in Dorset ($p = 0.77$). Thus, we did not find any significant correlation between total solar radiation and increasing DOC in Dorset. In NS, total solar radiation and DOC both had a weak upward trend (Fig. 3.1, Fig. 3.3B). However, total solar radiation typically exerts a negative effect on DOC concentration through photodecomposition processes (Hudson et al. 2003; Zhang et al. 2010; Couture et al. 2012; Sharpless and Blough 2014; Koehler et al. 2014; Mopper et al. 2015). Therefore, this relationship may be spurious. Although total solar radiation showed a downward pattern at the ELA (Fig. 3.2B), the correlation was weak (Pearson's correlation coefficient, $r = 0.35$, $p = 0.05$).

The effects of declining SO_4 deposition on the long-term patterns in DOC at Dorset and NS became apparent well after the emission control programs were in place in North America. And only after 2000, did the effects of SO_4 deposition on DOC pattern become evident. However, once evident, it is likely that the decrease in SO_4 deposition became a dominant factor that diminished the effects of other climate variables, such as solar radiation.

The declining pattern in SO₄ deposition is likely to stop in the near future. It may become constant over time and reach a new equilibrium within each watershed. However, future climate is unlikely to become stable, and climate variables are expected to continue to change. For example, studies have projected that warming may persist over the current century in Canada (Environment and Climate Change Canada 2016). Such an increase in temperature will also be apparent in eastern Canada (Ahmadi-Nedushan et al. 2007; Dugdale et al. 2018). Moreover, future precipitation in Canada may exhibit significant changes (Environment and Climate Change Canada 2016). Precipitation extremes have also been projected to increase over Canada (Zhou et al. 2018). In addition, stratospheric ozone recovery may be significantly delayed (Pommereau et al. 2018), which may increase the UV radiation in the future. Therefore, future DOC patterns may be affected by ongoing changes in climate variables and not as much by SO₄ deposition. We predict that if SO₄ deposition becomes constant over time, the climate variables may return as the most important correlates. Future studies should examine the relationship between DOC and climate variables in the absence of an effect of declining SO₄ deposition with longer dataset.

3.4.5 Relationship between DOC and the global explanatory variables

Few studies have included global variables in their analyses with DOC. Those studies that included global variables (e.g., Hudson et al. 2003; Zhang et al. 2010) found these variables were largely unrelated to DOC at most of their study sites. Only at the Turkey Lake Watershed, did Zhang et al. (2010) find a relationship between the long-term pattern in DOC, and SOI and PDO, but not at Dorset and NS sites. However, the correlation between DOC and global variables at the Turkey Lakes Watershed was weak. Surprisingly, we have observed stronger negative relationships between the global variables (i.e., NAO and PDO) and the long-term DOC

patterns at Dorset and NS. An explanation for the relationship between NAO and DOC may likely be found by examining the relationship between NAO and the regional climate variables.

A negative relationship between NAO and temperature has been reported across eastern Canada (Shabbar et al. 1997; Bonsal et al. 2001; Iles and Hegerl 2017), where NAO explained considerable winter temperature variability. A downward trend in NAO has been associated with warmer winter temperatures in eastern Canada and vice versa (Shabbar et al. 1997; Bonsal et al. 2001). A similar but weaker relationship was also observed between summer temperature and NAO. A downward trend in the summer NAO between 1988 and 2012 was associated with a warming in Eastern Canada (Iles and Hegerl 2017).

The relationship we have observed between long-term patterns in NAO and temperature in our study are consistent with past studies. A downward summer NAO trend was associated with a significant increase in summer temperature in Dorset (Fig. 3.9A-B). A similar relationship was also observed during the ice-free period (April to November) in NS (Fig. 3.10A-B). This increase in temperature could possibly contribute to an increase in the DOC concentration in Dorset and NS, as discussed earlier.

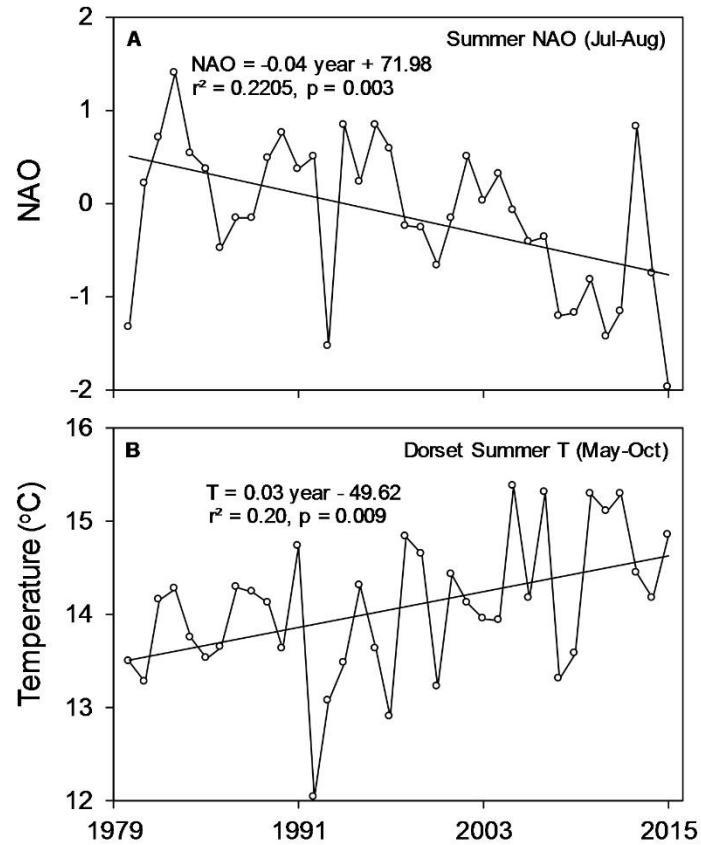


Figure 3.9. Long-term trends in summer NAO (July to August) and summer temperature at Dorset (May to October). Summer NAO showed a decreasing pattern over the study period (A). Associated with this decline in NAO was an increase in summer temperature in Dorset over the study period (B).

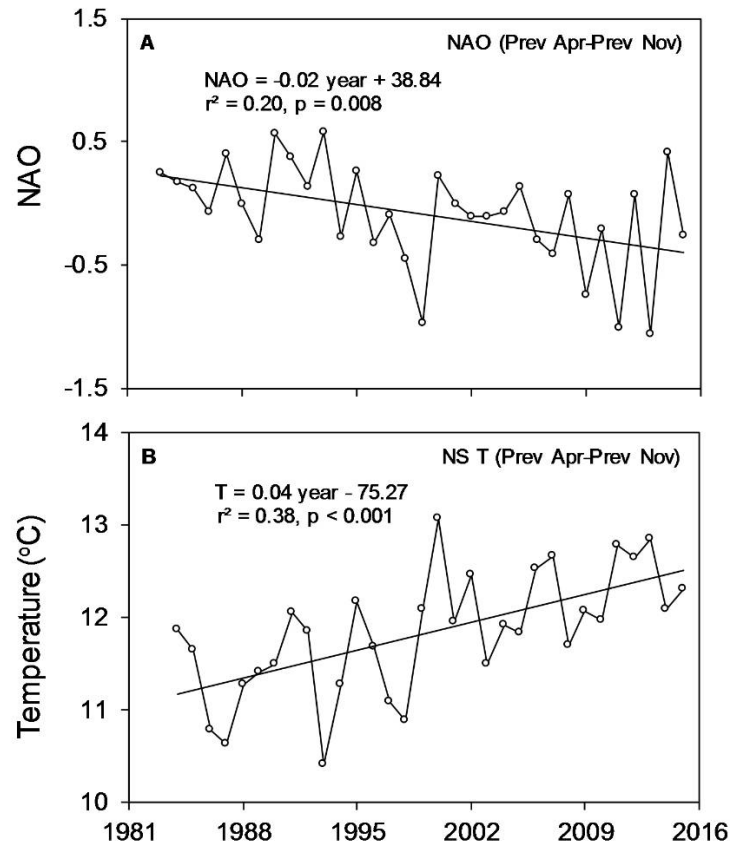


Figure 3.10. Long-term trends in NAO (previous year's ice-free period) and temperature (previous year's ice-free period) at Nova Scotia (NS). Ice-free period NAO showed a decreasing pattern over the study period (A). Associated with this decline in NAO was an increase in temperature at the NS site over the study period (B).

PDO was another global variable that was selected in the best and competing models for Dorset. PDO had a downward pattern over the study period and thus, a negative relationship with DOC at Dorset (Table 3.4, Fig. 3.5D). Although PDO was selected in the models, the amount of variation in DOC explained by PDO was low (Table 3.4). Past studies did not find any evident PDO effects in eastern Canada and most of the PDO effects were only confined to western Canada (Mantua et al. 1997; Bonsal et al. 2001; Mantua and Hare 2002; Whitfield et al. 2010; Bonsal and Shabbar 2011). Furthermore, we did not find a significant correlation between PDO and various time periods of temperature and precipitation that could possibly explain the PDO

effects on DOC in Dorset (as we did with NAO). PDO cycles are very long and usually persist for 20 to 30 years (Bonsal and Shabbar 2011). Perhaps the 36-year dataset in Dorset consisting of only 1 PDO cycle was not sufficient to capture the relationship that may exist between DOC and PDO in eastern Canada. Therefore, we encourage further investigation with a longer dataset that includes multiple PDO cycles.

3.4.6 Exceptions at the ELA

The long-term pattern in DOC at the ELA is distinct from that of Dorset and NS. Zhang et al. (2010) found an increasing DOC trend only at the ELA during their study period (1983-2002). However, this increasing trend did not continue over the last two decades. In fact, neither an increasing, nor a decreasing trend is evident in recent years. To isolate when a rise in DOC concentration stopped in the long-term DOC pattern, a piecewise regression was completed on the entire dataset. DOC concentration at the ELA increased up to 2000 ($p = 0.005$) and then stopped rising ($p = 0.59$, Fig. 3.11, Table 3.5).

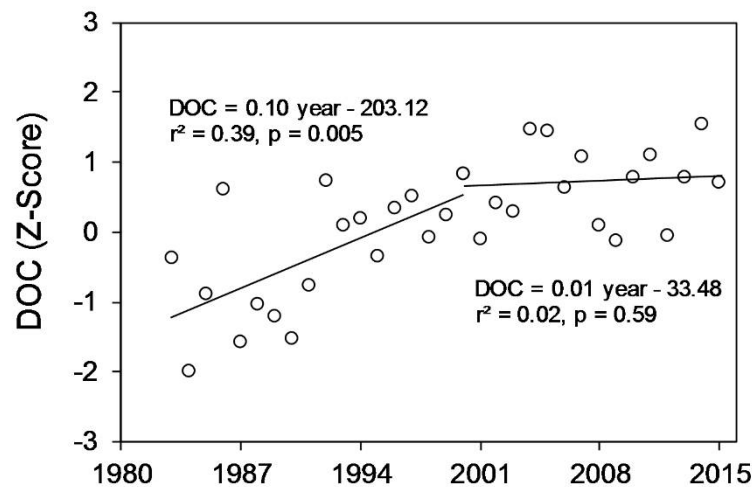


Figure 3.11. Two different DOC patterns were observed at the ELA between 1983 and 2015. A significant increase in DOC concentration was observed from 1983 to 2000. After 2000, however, a decreasing or increasing trend was not detected.

Table 3.5. Summary of separate DOC models produced from piecewise regression for the years between 1983 and 2000, and for the years between 2001 and 2015 at the ELA. The piecewise regression model for the entire dataset is: $\text{DOC} = -204.44 + 0.10 \text{ year} - 0.07 (\text{year} - 2000) D$. The value of the dummy variable (D) is zero (0) for the years between 1983 and 2000. The value of D is 1 for the years after 2000. “Not significant” is denoted by “ns”.

Year	Piecewise regression model	R ²	p value
1983-2000	$\text{DOC} = -204.44 + 0.10 \text{ year}$	0.53	< 0.001
2001-2015	$\text{DOC} = -204.44 + 0.10 \text{ year} - 0.07 (\text{year} - 2000)$	0.53	ns

Zhang et al. (2010) found that summer precipitation and total solar radiation were the most important explanatory variables that explained the long-term DOC pattern at the ELA, as well as, in other eastern Canadian sites. With a longer 33-year dataset, declining SO₄ deposition became the most important explanatory variable at the ELA. The difference between the two studies could be due to the lagged effect of declining SO₄ deposition. As noted earlier, sulfur emission control programs were initiated at the U.S. and Canada in the early 1980s, but the full implementation was gradual. In Canada, the programs were fully implemented by 1994 when the emission dropped from 4.6 million metric tons in 1980 to 2.4 million metric tons, which was well below the national cap of 3.2 million metric tons (Environment Canada 1996; Environment and Climate Change Canada 2017). However, due to the transboundary winds, sulfur emitted by U.S. could also affect the Canadian landscapes. The U.S. achieved its target of decreasing the sulfur emission by 9.1 million metric tons from the 1980 emission level by 2000 (Environment Canada 2014). Hence, sulfur emission reduction targets were met much later than the start of the programs. Furthermore, declining SO₄ deposition could take decades to become a dominant

factor because of the effects of previously stored sulfur from soils (Dillon et al. 1997; Mitchell et al. 2011; Garmo et al. 2014). The study period of Zhang et al. (2010) may not have captured the delayed effect of declining SO_4 deposition on DOC because a large portion of their study period includes years before the full implementation of emission control programs.

In our longer dataset, DOC was still weakly correlated with precipitation and total solar radiation at the ELA (Pearson's correlation coefficient, $0.35 \leq r \leq 0.48$, $0.004 \leq p \leq 0.04$). However, the effects of precipitation and total solar radiation on DOC pattern became insignificant once the effects from declining SO_4 deposition became dominant.

SO_4 deposition has continued to decline at the ELA during our study period, but DOC concentration has not continued to increase. The long-term pattern in DOC at the ELA lakes may have reached equilibrium in 2000 (Fig. 3.11), when DOC concentration did not increase in response to a further reduction in SO_4 deposition. Therefore, despite declining SO_4 deposition why an increasing DOC trend was not apparent? An explanation may exist. The pH in the ELA study lakes increased significantly between 1980 and 1991 (Fig. 3.8C) with a concomitant decline in SO_4 deposition (Fig. 3.2C). After 1991, the rate of decline in SO_4 deposition has slowed and pH slightly decreased till 2000. However, pH did not rise or decline significantly between 2001 and 2015. This may suggest that declining SO_4 deposition may now be insufficient to continue to cause an increase in pH and in turn, an increase in DOC concentration.

The long-term DOC pattern at the ELA may also be associated with the acidity caused by increased nitrogen (N) or ammonium (NH_4^+) deposition. The NH_4^+ deposition has doubled at the ELA since the early 1990s (Venkiteswaran et al. 2017). This increase in NH_4^+ deposition is associated with the intensification of agriculture in adjacent Manitoba which is upwind of the ELA (Venkiteswaran et al. 2017). Nitrogen (N) deposition has also increased in other Prairie

provinces in Canada (Hember 2018), which can also affect the downwind ELA site. Nitrogen addition can cause an increase in soil acidity from increased nitrification (Ye et al. 2018). Ammonium (NH_4^+) ions can dislocate base cations (e.g., Ca^{2+} , Mg^{2+} , K^+ , Na^+) and cause them to leach out of soils and hence, decrease the buffering capacity against acidification (Matchonats and Matzner 1996; Tian and Niu 2015). Additionally, with the absorption of NH_4^+ by plant roots, H^+ ions are released to the soil which may cause further acidification (Matson et al. 1999; Smith and Read 2008; Guo et al. 2010). The added acidity due to increasing N or NH_4^+ deposition may be offsetting the effect of declining SO_4 deposition, resulting in a relatively stable pH at the ELA in last two decades (Fig. 3.8C). Inclusion of long-term N or NH_4^+ deposition may increase the explained variation in DOC at the ELA. Therefore, we recommend that future studies should consider incorporating N and NH_4^+ deposition into their analysis.

Lastly, why are DOC concentrations still increasing (up to 2015) at Dorset and NS sites when DOC at the ELA has ceased to increase? The explanation may be attributed to the lower amount of N deposition at the Dorset and NS sites. As discussed earlier, N deposition has increased significantly at the ELA, where dissolved inorganic N (DIN; $\text{NO}_3^- + \text{NH}_4^+$) deposition and total N (TN) deposition were reported to be 5.4 and 6.7 kg N ha⁻¹ year⁻¹, respectively (Venkiteswaran et al. 2017). On the other hand, Hember (2018) reported that TN deposition in other boreal shield sites was 4.2 kg N ha⁻¹ year⁻¹ and exhibited a decline (-21%) between 1990 and 2013. Thus, the acidity from N deposition is likely lower and possibly declining at the Dorset and NS sites. Therefore, declining SO_4 deposition has likely remained a dominant factor at the Dorset and NS sites. This, in turn, has resulted in an increase in pH at Dorset and NS (Fig. 3.8A-B), and an increase in DOC concentration (Fig. 3.1B) over the last two decades.

3.5 Conclusion

Our results provide new insights into the long-term patterns in DOC in eastern Canadian lakes. There was a considerable increase in the DOC concentration in Dorset and NS (Kejimikujik and Yarmouth) in the last two decades. At the ELA, although DOC concentration increased initially, an increasing or decreasing pattern was not evident in the last two decades. Declining SO_4 deposition was found to be the most important explanatory variable in eastern Canadian lakes. Precipitation also explained a considerable amount of variation in DOC in Dorset and NS. Global variables (e.g., NAO and PDO) emerged as significant explanatory variables in these longer datasets.

We have identified other potential regional variables (i.e., N or NH_4^+ deposition) that may influence long-term patterns in DOC in lakes. We recommend further long-term monitoring to determine when DOC patterns in Dorset, NS and other lakes worldwide may stop rising as we observed at the ELA. Finally, in agreement with Zhang et al. (2010), we encourage testing of these correlational studies with more extensive datasets that may capture new patterns in DOC. Longer datasets would also be useful to further clarify the relationship of global variables (e.g., PDO) with long-term patterns in DOC.

CHAPTER 4. SUMMARY

4.1 Long-term patterns in DOC at each study site

Dissolved organic carbon (DOC) is an important water quality parameter that contributes to many aquatic ecosystem processes. For example, DOC can serve as a source of energy; affect the solubility and availability of metals and nutrients; attenuate ultraviolet radiation; affect water transparency and thermal stratification; reflect watershed characteristics, and so forth. Long-term DOC patterns in forty-nine lakes from four eastern Canadian sites were analyzed over a ~35-year period. The study sites were Kejimikujik, Yarmouth, Dorset and the Experimental Lakes Area (ELA). Long-term DOC patterns in lakes showed a temporally coherent pattern within a site. Therefore, a mean regional pattern was established and used to represent the long-term DOC pattern of a site. However, DOC patterns were not temporally coherent across sites, except between Kejimikujik and Yarmouth. In addition, all the regional variables (i.e., precipitation, temperature, total solar radiation, sulfate deposition) were only temporally coherent between Kejimikujik and Yarmouth. This is because of the close proximity of the two sites. Therefore, Kejimikujik and Yarmouth were pooled into a single Nova Scotia (NS) site.

Evidence to support an increasing or decreasing trend in Dorset and NS was not present from early 1980s to late 1990s. However, an increase in DOC concentration in the Dorset lakes was evident between 1997 and 2015 (increase of $0.12 \text{ mg L}^{-1} \text{ year}^{-1}$, $r^2 = 0.68$, $p < 0.001$). Likewise, increases in DOC concentration were also apparent between 2000 and 2015 in Kejimikujik lakes (increase of $0.12 \text{ mg L}^{-1} \text{ year}^{-1}$, $r^2 = 0.42$, $p = 0.007$), and Yarmouth lakes (increase of $0.11 \text{ mg L}^{-1} \text{ year}^{-1}$, $r^2 = 0.30$, $p = 0.03$). The combined site, NS also showed a similar increasing pattern in the last two decades (increase of $0.11 \text{ mg L}^{-1} \text{ year}^{-1}$, $r^2 = 0.34$, $p = 0.02$). The long-term DOC pattern at the ELA study lakes was more complex. There was an increasing trend

in the ELA study lakes between 1983 and 2000 (increase of $0.10 \text{ mg L}^{-1} \text{ year}^{-1}$, $r^2 = 0.39$, $p = 0.005$). However, this increase was not present during the last two decades, and evidence of an increase or decrease in DOC was not detected between 2001 and 2015 ($p = 0.59$).

4.2 Important explanatory variables at each site

Multiple linear regression (MLR) analysis was conducted to analyze the relationship between DOC concentration and a set of explanatory variables (regional and global). Akaike's information criteria (AIC) was used to select the most parsimonious and competing model(s) at each site. Two best models were selected for the Dorset site from these analyses. The best model explained 75% variation in long-term DOC pattern and the competing model explained 80% variation. The models in Dorset included two regional variables: precipitation and sulfate (SO_4) deposition, and two global variables: North Atlantic Oscillation (NAO) and Pacific Decadal Oscillation (PDO). A single best model was selected for the NS sites that explained 88% of the variation in the long-term pattern in DOC. The model included precipitation, SO_4 deposition, temperature and NAO. The best model that was selected at the ELA explained 47% of the variation in the long-term DOC pattern. The model included SO_4 deposition and temperature.

This analysis revealed that the decline in SO_4 deposition was the most important explanatory variables to describe the long-term pattern in DOC in eastern Canadian lakes. Increases in DOC concentration reported in the literature for other sites have largely been attributed to declining SO_4 deposition (Monteith et al. 2007; Erlandsson et al. 2008; Hruska et al. 2009; Haaland et al. 2010; SanClements et al. 2012). Decreased acidity due to declining SO_4 deposition may increase DOC concentration by increasing soil pH, and by decreasing the mobilization of aluminum that may bind with DOC. Declining SO_4 deposition can also reduce the multivalent ions (e.g., Ca^{2+} , Mg^{2+}) which can considerably reduce the ionic strength in soil.

This, in turn, can accelerate the export of allochthonous DOC from the landscape to waters. A decline in SO_4 deposition can result in an increase in lake pH, and therefore, reduce the rate of acid-enhanced photo-degradation of DOC (Gennings et al. 2001; Kohler et al. 2002; Molot et al. 2005).

Precipitation explained a significant amount of variation in the long-term patterns in DOC at Dorset and NS. There was a positive relationship between DOC and precipitation at both sites. Because of a strong association between DOC export and runoff, an increase in precipitation can cause a significant loss from the terrestrial organic carbon pool and therefore, increase the DOC export from terrestrial to aquatic systems (Dyson et al. 2011; Yoon and Raymond 2012; Qiao et al. 2017). Although heavy precipitation can exert a negative dilution effect on DOC concentration (Li et al. 2016), this was not observed in our study sites.

Temperature was one of the most important explanatory variables at the NS and the ELA sites. In NS, there was a positive relationship between DOC and temperature. An increase in temperature may increase DOC concentration in peat soils, and subsequently in water, by increasing decomposition rates via microbial processes (Freeman et al. 2001). However, we observed a negative relationship between DOC and temperature at the ELA. A decline in flow associated with rising temperature could result in a reduced export of DOC from catchments (Schindler et al. 1996). Decreased flow and increased evaporation at the lake surface due to higher temperatures could increase the water retention time in lakes. This could increase the exposure of DOC to photochemical and microbial removal processes, and consequently, reduce DOC concentration (Schindler et al. 1996). Furthermore, DOC concentration can also decrease from an increase in the rates of bacterial mineralization and photodegradation that comes with an increase in temperature (Shirokova et al. 2013).

Interestingly, some global variables (i.e., NAO and PDO) were selected in the best model and the competing models in Dorset and NS. There was a negative relationship between DOC and NAO at Dorset and NS. This relationship could be explained by examining the relationship between NAO and temperature. A negative relationship between NAO and temperature has been reported across eastern Canada (Bonsal et al. 2001; Iles and Hegerl 2017). In Dorset, a downward summer NAO trend was associated with a significant increase in summer temperature. A similar association was also observed between NAO and temperature in NS during the ice-free period of the previous year. This increase in temperature at both sites could be related to the increase in DOC concentration.

PDO was selected in the both models at Dorset, where PDO had a negative relationship with DOC. However, we did not find a significant correlation between PDO and various time periods of temperature and precipitation that could possibly explain the PDO effects on DOC in Dorset (as we did with NAO).

4.3 Comparison with past studies

We observed significant changes in the long-term patterns in DOC in eastern Canadian lakes since the last study of Zhang et al. (2010). For example, Zhang et al. (2010) did not find any evidence to support an increasing or decreasing DOC pattern in Dorset and NS with their 21-year dataset. However, with an additional 15 years of data, we observed an increasing DOC pattern at these sites in the last two decades. Zhang et al. (2010) only found an increasing pattern at the ELA. However, a general increase or decrease in DOC at the ELA was not apparent between 2001 and 2015 in the current study.

Past studies reported increases in DOC concentration at many European and North American sites starting from late 1980s and early 1990s (e.g., Bouchard 1997; Forsius et al.

2003; Driscoll et al. 2003; Evans et al. 2005). These increases were mostly associated with the recovery of watersheds from acidification that resulted from a decline in SO₄ deposition. However, in Dorset and NS, DOC concentration only started to increase in the late 1990s, despite a declining rate of SO₄ deposition that started in the early 1980s. Recovery from acidification in Dorset and NS may have been delayed from the release and oxidation of internal sulfur in catchments that was previously stored in soil during the high SO₄ deposition years (Dillon et al. 1997; Watmough et al. 2005; Mitchell et al. 2011; Garmo et al. 2014). Also, less acid buffering capacity in Dorset and NS watershed soils could have delayed the recovery. As a result, changes in SO₄ deposition could take decades to affect the DOC concentration in lakes.

Furthermore, differences in the related explanatory variables are evident between the Zhang et al. (2010) study and this study. In the current study, declining SO₄ deposition was the most important explanatory variable. However, precipitation and total solar radiation were the most important explanatory variables in the study of Zhang et al. (2010). This could be a result of the absence of an increasing DOC pattern (except for ELA) in their study. In addition, although the sulfur emission control programs were initiated in early 1980s, targets were met in Canada and U.S. by 1994 and 2000; respectively. Possibly, SO₄ deposition did not appear as an important explanatory variable in Zhang et al. (2010) study because a large portion of their 21-year dataset includes years before the sulfur emission control programs were fully implemented.

With additional 15 years of data, precipitation was still an important explanatory variable in NS and Dorset, but total solar radiation was not. In our longer dataset, DOC still had some significant, but weaker correlations with precipitation and total solar radiation at the ELA. However, once the decline in SO₄ deposition started to significantly affect the DOC

concentration, the effects of total solar radiation and precipitation may have become less significant.

The increases in DOC worldwide is now well documented. However, the end of the DOC increase at the ELA is unique. The long-term pattern in DOC at the ELA lakes may have reached equilibrium in 2000, when DOC concentration did not increase in response to any further reductions in SO_4 deposition. This may suggest that the declining SO_4 deposition may now be insufficient to cause further increases in DOC concentration. A contributing factor that may prevent further increases in DOC at the ELA may be related to the deposition of another landscape acidifying agent, nitrogen (N), particularly ammonium (NH_4^+). NH_4^+ deposition has doubled in the ELA in last 45 years due to an intensification of agriculture in adjacent Manitoba (Venkiteswaran et al. 2017). Ammonium (NH_4^+) ions can decrease the buffering capacity against acidification by dislocating the base cations (e.g., Ca^{2+} , K^+ , Na^+) and causing them to leach out of soils (Matchonats and Matzner 1996; Tian and Niu 2015). Additionally, with the absorption of NH_4^+ , plant roots release H^+ ions to the soil which may also cause acidification (Matson et al. 1999; Smith and Read 2008; Guo et al. 2010). Nitrogen addition can also increase soil acidity by causing an increase in nitrification (Ye et al. 2018). Therefore, increased acidity due to increasing NH_4^+ and N deposition may be offsetting the effect of declining SO_4 deposition on the landscapes and in the ELA waterbodies. This would halt any further increases in the DOC as seen at the ELA in the last two decades.

Past studies that included global variables in analyses (e.g., Hudson et al. 2003; Zhang et al. 2010) found them to be largely unrelated to DOC. Surprisingly, some global variables (i.e., NAO and PDO) have emerged as important explanatory variables for the long-term patterns in DOC at Dorset and NS. These global variables have long cycles that may persist for 20 to 30

years. A longer dataset that includes multiple cycles of these global variables, may be required to isolate relevant relationships. In the shorter studies of Hudson et al. (2003) and Zhang et al. (2010), the study period (21 year) may not have been sufficient for the global variables to emerge as the explanatory variables.

4.4 Implication of observed results

Recent increases in DOC concentration in eastern Canadian lakes may have ecological consequences. An increase in DOC concentration may affect the balance between photosynthesis and respiration in lakes by attenuating solar radiation (von Einem and Graneli 2010; Kritzberg et al. 2014, Kelly et al. 2014) and thus, restrict primary productivity (Jones et al. 2012; Thrane et al. 2014; Seekell et al. 2015), and in turn, may reduce invertebrate and fish production in our study sites (Karlsson et al. 2009; Kelly et al. 2014; Benoit et al. 2016). An increase in light attenuation might also result in an increase in the release of reactive oxygen species (ROS) and free radicals, which can negatively impact aquatic biota (Dalrymple et al. 2010; Zhang et al., 2014; Krumova and Cosa 2016; Wolf et al. 2018). The decrease in water transparency due to the increase in DOC may alter thermal stratification in lakes (Williamson et al. 2015; Strock et al. 2017; Pilla et al. 2018). Because of DOC's high binding capacity, an increase in DOC may affect the mobility and toxicity of metals in our study sites (French et al. 2014; Braaten et al. 2018). An increase in DOC concentrations in eastern Canadian lakes can also be a human health concern. Higher DOC concentrations can increase the treatment cost of surface waters that are used for drinking (Hongve et al. 2004; Ritson et al. 2014). During the treatment process, increased DOC can also interact with chlorine to produce carcinogenic trihalomethanes (Chowdhury 2018).

However, it is also known that an increase in DOC can stimulate primary production when nutrients bound with the DOC are released by photodegradation process (Sereda et al.

2012; Kissman et al. 2013). A greater concentration in DOC may also promote primary production by providing better protection from UVR and by increasing the concentration of dissolved CO₂ through enhanced photo and bacterial mineralization (Jansson et al. 2012; Lapierre et al. 2013).

4.5 Future direction

Future studies should include more extensive datasets to analyze the long-term patterns in DOC. Longer records would help to identify the association between DOC and global variables because the global variables usually have long cycles (e.g., PDO has a cycle of 20 to 30 years). With a ~35-year dataset, we could not explain the association between DOC and PDO in eastern Canadian lakes. Perhaps, a more longer dataset consisting of two or three PDO cycles would be required to explain such relationships. We also recommend continuing further monitoring of DOC concentrations to capture any future changes at our study sites. For example, continued monitoring is imperative to determine if the current pattern in DOC in Dorset and NS lakes will stop rising as seen at the ELA. We recommend that future studies should also consider including additional variables in their sampling programs (specifically, N or NH₄⁺ deposition).

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